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Ligand displacement reactions of dimer and trimer pyridyl ligand/transition metal complexes

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Abstract

Ligand exchange reactions of pyridyl ligand/transition metal complexes are examined in a quadrupole ion trap mass spectrometer to evaluate the ability of multidentate ligands to displace other pyridyl ligands in complexes where the charge is highly delocalized and there is a great degree of ligand repulsions. Partially or fully coordinated transition metal ions in dimer or trimer species involving small mono- or bidentate pyridyl ligands undergo ligand displacement reactions with larger bi- and tridentate pyridyl ligands. Larger ligands with greater chelation abilities, such as 1,10-phenanthroline and 2,2′:6,2″-terpyridine, are often able to simultaneously displace two nonchelating ligands from a partially coordinated metal ion. However, the analogous reactions involving displacement of bidentate chelating ligands from more fully coordinated transition metal ion complexes are nearly quenched. In other cases, mixed-ligand dimer and trimer complexes are observed, indicating step-wise displacement of the initially complexed ligands. (Int J Mass Spectrom 182/183 (1999) 311–322) © 1999 Elsevier Science B.V.

1. Introduction

Coordination chemistry in solution plays an enormous role in many areas of science including metalloenzyme activities [1], biointeractions of pharmaceuticals [2], environmental chemistry [3], and reaction catalysis [4]. For example, metal ions often play a key role in holding substrates in proper orientations for subsequent reactions with other organic molecules. Studies of metal complexation in the gas phase allow the examination of intrinsic aspects of the formation of organometallic and inorganic complexes in the absence of solvation [5–17]. Formation of multiligand metal complexes is influenced by the size and chelating abilities of the ligands and the size and electronic nature of the metal ion. Systematic studies of metal complexation and ligand displacement reactions assist the understanding of the factors that dictate both binding selectivities and binding strengths of organic ligands. In this article, we continue our ongoing studies of multiligand metal coordination in the gas phase with an emphasis on ligand displacement reactions involving multidentate pyridyl ligands, thus allowing detailed study of how chelating ligands react with metal ions that are already partially or fully coordinated.

In solution, chelating ligands are able to bind metal ions more strongly than multiple nonchelating ligands with the same overall number of donor groups be-

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Dedicated to the memory of Ben Freiser to commemorate his many seminal contributions to mass spectrometry and gas phase ion chemistry.

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cause of the chelate effect [18,19]. A metal ion already attached to one binding site of a multidentate ligand is more likely to be complexed by the other binding sites on that ligand because of their close proximity to the ion. In addition, a metal ion coordinated at multiple sites by one ligand leaves more independent ligands in solution than coordination by multiple ligands and thus leaves an overall more favorable entropy situation. In solution chelating ligands having the same donor groups typically displace nonchelating ligands already bound to guest compounds. This study examines the displacement reactions of chelating versus nonchelating ligands in the absence of solution. Factors such as the identity, number, and position of ligand donor atoms affect the ability of a given ligand to bind and engage in multisite coordination or chelation with a metal ion. In addition, the size and polarizability of the ligands influence binding ability when no solvents are present. Previous studies in the gas phase have examined complex formation between simple model compounds such as polyethers and pyridyl ligands and a series of monopositive metal ions. Degree of higher order complex formation (i.e. formation of dimers and trimers) and metal ion free binding energies were determined for both single-ligand and mixed-ligand complexes [11,12]. Other studies have focussed on measuring metal-ligand bond energies, finding that after the first ligands are attached, the binding energy generally decreases as each additional coordinated ligand is added [9,10].

The pyridyl ligands, including pyridine, 2,2′-dipyridine, 4,4′-dipyridine, 1,10-phenanthroline, and 2,2′:6′,2″-terpyridine, were used in this study along with the transition metal ions Co^+, Ni^+, and Cu^+ to examine higher order ligand complex binding strengths and ligand displacement. The pyridyl ligands are excellent model compounds to study these aspects of metal complexation because they all contain the same nitrogen donor atoms which allow binding to the metal but vary in the number of donor atoms, size, flexibility, and chelating ability. Furthermore, each ligand in a given dimer or trimer complex will have a different binding free energy dependent on the degree of ligand repulsions. Ligand exchange experiments involving only single-ligand complexes have been performed previously to analyze metal binding free energies, and it was shown that the binding free energies correlate well with the *n*-dentate nature of the ligand [11]. However, it was not straightforward to separate how factors such as flexibility and size influenced, for example, the ability of bidentate 2,2′-dipyridine to displace the monodentate pyridine from a $[\text{pyridine}_2 \cdot M^+]$ complex, where M^+ is one of the transition metal ions complexed to two pyridine ligands. The present study utilizes the same ligand exchange techniques to examine higher order ligand complexes and ligand displacement. For example, a metal complex containing two or three of one given ligand is isolated and allowed to react with another neutral ligand. Identification of mixed-ligand product complexes containing one or more of each ligand and relative abundances of the complexes permit some insight into the mechanism of ligand displacement. The key parameters directing the displacement can be inferred from the products observed, such as resultant product stability because of the ability of the complexing ligand to orient itself optimally to the metal and the overall degree of metal coordination. In this way a two ligand metal complex composed of two monodentate ligands can be compared directly to a single ligand complex containing one bidentate ligand, where the degree of metal coordination remains the same but the chelating abilities of the ligands differ. For example, the ability of the flexible bidentate 2,2′-dipyridine can be evaluated against the ability of the rigid bidentate 1,10-phenanthroline to displace the monodentate pyridine from a $[\text{pyridine}_2 \cdot M^+]$ complex, where the metal ion is already complexed at two sites.

2. Experimental

All experiments were performed in a Finnigan quadrupole ion trap mass spectrometer [20] fitted with a probe-mounted fiber optic laser desorption assembly [21]. Solid compounds were admitted into the trap via a temperature-controlled solids probe operated at 30–80 °C, while low boiling pyridine was admitted through a leak valve to a nominal pressure of 10^{-6} Torr. Two pyridyl ligands were introduced into the trap simultaneously using one probe (or leak valve) for each ligand. The concentrations of the two ligands were adjusted in order to be approximately equal. When it was difficult to estimate concentrations based on pressures, the analytes were assumed to be at the same concentrations when mass spectral intensities of their electron ionization (EI) spectra were similar. The ligands were allowed to react with a laser desorbed metal ion (Co^+, Ni^+, or Cu^+) and an array of complexes were formed. One pyridyl ligand-transition metal complex of interest was isolated and allowed to react further with the two neutral ligands still present in the vacuum chamber at nearly equimolar concentrations, thus, allowing both types of neutral ligands to interact with the isolated complex. The resulting complexes were analyzed to determine if and to what extent the ligands initially associated with the metal could be displaced by the other ligands present. The products resulting from the reaction were monitored. The complexes were mass-analyzed by operating the ion trap in the mass-selective instability mode. Helium was used as the buffer gas and maintained at a pressure of nominally 8×10^{-5} Torr (about 1 mTorr).

Transition metal ions were generated by ablation of metal foils with a pulsed Nd:YAG laser. The laser was operated in the *Q*-switch mode with a power density of 2×10^8 W/cm^2. The metal ions were stored in the ion trap and allowed to react with the neutral pyridyl ligands as described previously. It is possible that some of the metal ions existed in excited states because the laser desorption event deposits a large amount of energy to the metal foil. Therefore, the results reported may reflect the product distributions arising from metal ions in both ground and excited electronic states. However, previous work from this group suggests the metal ions behave reproducibly at a number of different pressures and laser power settings. If ions do exist in different states, no experimental differences in product distributions could be determined. Because no experimental irregularities were observed in the present study either, the presence of excited states is not addressed further.

All compounds and transition metal foils were obtained from Aldrich Chemical Co. (Milwaukee, WI) except 2,2′-dipyridine which came from Sigma Chemical Co. (St. Louis, MO). All were used without further purification.

3. Results and discussion

3.1. Overview of strategy

Ligand exchange reactions offer an effective way to probe the strength of metal-ligand binding interactions in the gas phase, especially for complexes in which the metal ion is coordinated by several ligands, where each ligand does not have the same binding energy. The strategy used in this study entails the examination of ligand exchange reactions involving metal complexes in which the metal ion is coordinated by two or three monodentate or bidentate pyridyl ligands and allowed to react with other monodentate, bidentate, or tridentate pyridyl ligands. The displacement of the initial pyridyl ligands is monitored, with special interest in detecting the presence of stable mixed-ligand complexes. The initial metal complexes were produced by allowing monopositive metal ions, formed by laser ablation of a metal foil, to react with one of the ligands, pyridine, 4,4′-dipyridine, or 2,2′-dipyridine. These three ligands were chosen because they have the weakest coordination strengths of the set of five pyridyl ligands shown in Fig. 1, so it is expected that some ligand displacement will occur in the ligand exchange reactions. The metal complex of interest is isolated and allowed to interact with a second ligand (2,2′-dipyridine, 4,4′-dipyridine, 1,10-phenanthroline or 2,2′:6′,2″-terpyridine). The abilities of the various multidentate pyridyl ligands to displace one or all of the initial pyridyl ligands were evaluated based on the product distributions after the ligand exchange reaction period.

The results of the ligand displacement reactions are summarized in Tables 1–3 and examples of the spectra are shown in Figs. 2–4. For example, the ligand exchange reactions between [pyridine$_2 \cdot Cu^+$] with 2,2′-dipyridine or 2,2′:6′,2″-terpyridine are

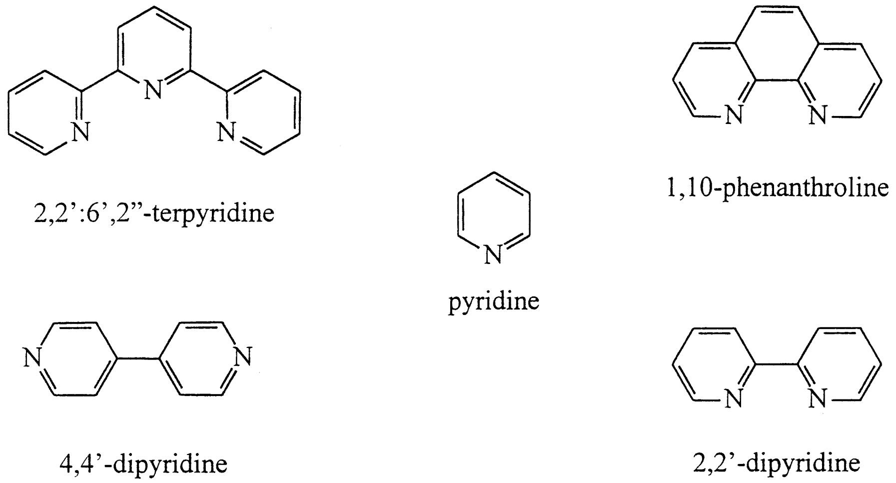

Fig. 1. Structures of pyridyl ligands studied.

shown in Figs. 2(A) and 2(B) and summarized in Table 1 in the last group of entries. Formation of the mixed-ligand [pyridine · 2,2′-dipyridine · Cu$^+$] complexes is favored upon reaction of 2,2′-dipyridine with [pyridine$_2$ · Cu$^+$] (Fig. 2(A)), whereas formation of stable mixed-ligand complexes is greatly suppressed upon reaction with 2,2′:6′,2″-terpyridine (Fig. 2(B)). Because the product distributions vary with

Table 1
Product distributions for ligand displacement reactions involving pyridine-transition metal complexes

Isolated complex								
Displacing ligand (L2)	Products formed[a]							
[pyridine$_2$ · Co$^+$]	**[pyr$_2$ · Co$^+$]**	[pyr · L2 · Co$^+$]	[L2$_2$ · Co$^+$]				[L2$_3$ · Co$^+$]	[L2 · Co$^+$]
2,2′-dipyridine	5	9	77				9	--
4,4′-dipyridine	34	52	14				x	--
1,10-phenanthroline	41	17	25				17	--
2,2′:6′,2″-terpyridine	34	27	37				x	2
[pyridine$_2$ · Ni$^+$]	**[pyr$_2$ · Ni$^+$]**	[pyr · L2 · Ni$^+$]	[L2$_2$ · Ni$^+$]	[pyr$_3$ · Ni$^+$]	[pyr$_2$ · L2 · Ni$^+$]	[pyr · L2$_2$ · Ni$^+$]	[L2$_3$ · Ni$^+$]	[L2 · Ni$^+$]
2,2′-dipyridine	18	36	27	19	--	--	x	--
4,4′-dipyridine	26	11	3	10	33	15	2	--
1,10-phenanthroline	34	29	31	6	--	--	x	--
2,2′:6′,2″-terpyridine	23	19	32	15	--	--	x	11
[pyridine$_3$ · Ni$^+$]		[pyr · L2 · Ni$^+$]	[L2$_2$ · Ni$^+$]	**[pyr$_3$ · Ni$^+$]**	[pyr$_2$ · L2 · Ni$^+$]	[pyr · L2$_2$ · Ni$^+$]	[L2$_3$ · Ni$^+$]	
2,2′-dipyridine		18	40	27	15	--	x	
4,4′-dipyridine		--	8	34	45	13	--	
1,10-phenanthroline		38	32	30	--	--	x	
2,2′:6′,2″-terpyridine		45	26	29	--	--	x	
[pyridine$_2$ · Cu$^+$]	**[pyr$_2$ · Cu$^+$]**	[pyr · L2 · Cu$^+$]	[L2$_2$ · Cu$^+$]					[L2 · Cu$^+$]
2,2′-dipyridine	38	39	23					--
4,4′-dipyridine	30	63	7					--
1,10-phenanthroline	36	34	30					--
2,2′:6′,2″-terpyridine	52	5	21					22

[a] Products are reported as a percentage of total ion intensity after the ligand exchange period. An x indicates the product does not form as previously reported by Wu and Brodbelt, 1995. A double dash indicates the product was not observed during this experiment. All values +/− 10%.

Table 2
Product distributions for ligand displacement reactions involving 2,2′-dipyridine-transition metal complexes

Isolated complex Displacing ligand (L2)	Products formed[a]						
$[2,2'\text{-dipyridine}_2 \cdot \text{Co}^+]$	**$[2,2'_2 \cdot \text{Co}^+]$**	$[2,2' \cdot \text{L2} \cdot \text{Co}^+]$	$[\text{L2}_2 \cdot \text{Co}^+]$	$[2,2'_3 \cdot \text{Co}^+]$	$[2,2'_2 \cdot \text{L2} \cdot \text{Co}^+]$	$[2,2' \cdot \text{L2}_2 \cdot \text{Co}^+]$	$[\text{L2}_3 \cdot \text{Co}^+]$
1,10-phenanthroline	25	30	13	14	9	5	4
2,2′:6′,2″-terpyridine	38	22	--	40	--	--	x
$[2,2'\text{-dipyridine}_3 \cdot \text{Co}^+]$		$[2,2' \cdot \text{L2} \cdot \text{Co}^+]$		**$[2,2'_3 \cdot \text{Co}^+]$**	$[2,2'_2 \cdot \text{L2} \cdot \text{Co}^+]$	$[2,2' \cdot \text{L2}_2 \cdot \text{Co}^+]$	$[\text{L2}_3 \cdot \text{Co}^+]$
1,10-phenanthroline		—		32	12	18	38
2,2′:6′,2″-terpyridine		12		88	--	--	x
$[2,2'\text{-dipyridine}_2 \cdot \text{Ni}^+]$	**$[2,2'_2 \cdot \text{Ni}^+]$**	$[2,2' \cdot \text{L2} \cdot \text{Ni}^+]$	$[\text{L2}_2 \cdot \text{Ni}^+]$				
1,10-phenanthroline	26	47	27				
2,2′:6′,2″-terpyridine	10	90	--				
$[2,2'\text{-dipyridine}_2 \cdot \text{Cu}^+]$	**$[2,2'_2 \cdot \text{Cu}^+]$**	$[2,2' \cdot \text{L2} \cdot \text{Cu}^+]$	$[\text{L2}_2 \cdot \text{Cu}^+]$				
1,10-phenanthroline	35	53	12				
2,2′:6′,2″-terpyridine	21	71	8				

[a] Products are reported as a percentage of total ion intensity after the ligand exchange period. An x indicates the product does not form as previously reported by Wu and Brodbelt, 1995. A double dash indicates the product was not observed during this experiment. All values ±10%.

time and are dependent on the concentrations of reactants, the relative product distributions are reported as semiquantitative percentages which are used to denote trends (Tables 1–3); small differences in percentages should not be used to overinterpret differences in the coordination strengths of the ligands.

In the following sections, the displacement reactions of each type of metal complex (i.e. containing either pyridine, 2,2′-dipyridine, or 4,4′-dipyridine molecules and either Co^+, Ni^+, or Cu^+) are described in greater detail, and the most significant trends are summarized in the conclusions. As noted from a previous study [11], Co^+ can be coordinated by up to two monodentate pyridyl ligands, three bidentate pyridyl ligands, or two tridentate pyridyl ligands. In contrast, Ni^+ can be coordinated by up to three monodentate pyridyl ligands, two bidentate pyridyl ligands, or two tridentate ligands. Finally, Cu^+ can be

Table 3
Product distributions for ligand displacement reactions involving 4,4′-dipyridine-transition metal complexes

Isolated complex Displacing ligand (L2)	Products formed[a]					
$[4,4'\text{-dipyridine}_2 \cdot \text{Co}^+]$	**$[4,4'_2 \cdot \text{Co}^+]$**	$[4,4' \cdot \text{L2} \cdot \text{Co}^+]$	$[\text{L2}_2 \cdot \text{Co}^+]$		$[\text{L2}_3 \cdot \text{Co}^+]$	
1,10-phenanthroline	29	32	27		12	
2,2′:6′,2″-terpyridine	28	55	17		x	
$[4,4'\text{-dipyridine}_2 \cdot \text{Ni}^+]$	**$[4,4'_2 \cdot \text{Ni}^+]$**	$[4,4' \cdot \text{L2} \cdot \text{Ni}^+]$	$[\text{L2}_2 \cdot \text{Ni}^+]$	$[4,4'_3 \cdot \text{Ni}^+]$		$[\text{L2} \cdot \text{Ni}^+]$
1,10-phenanthroline	21	42	18	19		--
2,2′:6′,2″-terpyridine	15	24	14	40		7
$[4,4'\text{-dipyridine}_3 \cdot \text{Ni}^+]$		$[4,4' \cdot \text{L2} \cdot \text{Ni}^+]$	$[\text{L2}_2 \cdot \text{Ni}^+]$	**$[4,4'_3 \cdot \text{Ni}^+]$**		
1,10-phenanthroline		35	22	43		
2,2′:6′,2″-terpyridine		36	34	30		
$[4,4'\text{-dipyridine}_2 \cdot \text{Cu}^+]$	**$[4,4'_2 \cdot \text{Cu}^+]$**	$[4,4' \cdot \text{L2} \cdot \text{Cu}^+]$	$[\text{L2}_2 \cdot \text{Cu}^+]$			$[\text{L2} \cdot \text{Cu}^+]$
1,10-phenanthroline	34	43	23			--
2,2′:6′,2″-terpyridine	46	8	34			12

[a] Products are reported as a percentage of total ion intensity after the ligand exchange period. An x indicates the product does not form as previously reported by Wu and Brodbelt, 1995. A double dash indicates the product was not observed during this experiment. All values ±10%.

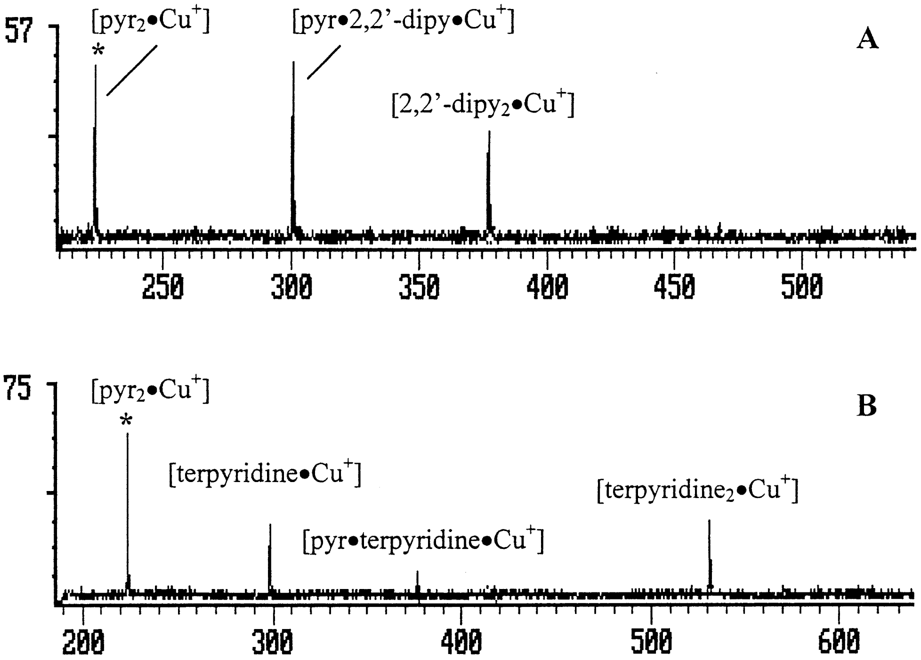

Fig. 2. Displacement of pyridine from an isolated [pyridine$_2$ · Cu$^+$] complex* with **(A)** 2,2′-dipyridine after 300 ms or **(B)** 2,2′:6,2″-terpyridine after 75 ms.

coordinated by up to two monodentate, bidentate or tridentate ligands. This previous study confirmed that there was an interplay between the number of coordination sites of the monopositive transition metal ion and the degree of ligand–ligand repulsions in the complexes. Thus, we were particularly interested to evaluate the number and types of ligands favored in the formation of mixed-ligand complexes. The most compelling result, as described in Sec. 3.3., involves the reactions of 2,2′:6′,2″-terpyridine with the fully coordinated [2,2′-dipyridine$_3$ · Co$^+$] complex, in which the tridentate ligand is unable to efficiently displace a bidentate ligand from the metal ion.

3.2. Displacement of pyridine

Pyridine is a small, single-ring, monodentate molecule which forms monomers and dimers with Co$^+$, Ni$^+$, and Cu$^+$ ions but forms trimers only with Ni$^+$ ions in the gas phase. Larger pyridyl ligands are able to displace pyridine from these dimers and trimers to various degrees as shown in Table 1. Of the displacing ligands listed, only 4,4′-dipyridine is also a nonchelator like pyridine. However, because of its larger size and polarizability it is still able to displace one or both pyridine molecules and form more stable complexes with these transition metals. 1,10-Phenanthroline is a large, rigid, bidentate compound, while 2,2′-dipyridine is a more flexible bidentate ligand of similar size. Both of these and the tridentate terpyridine are able to displace pyridine to form a variety of products, including mixed-ligand dimers and trimers.

As noted earlier, Co$^+$ is coordinated by up to two monodentate pyridyl ligands, three bidentate pyridyl ligands, or two tridentate pyridyl ligands in the gas phase [11]. The product distributions for reactions of [pyridine$_2$ · Co$^+$] with each of the four other pyridyl ligands (L2) are shown in the first set of entries in Table 1. As shown, stable mixed-ligand dimers, i.e. [pyridine · L2 · Co$^+$], are uniformly observed, but mixed-ligand trimers [pyridine$_2$ · L2 · Co$^+$] are never observed. This latter result is somewhat surprising

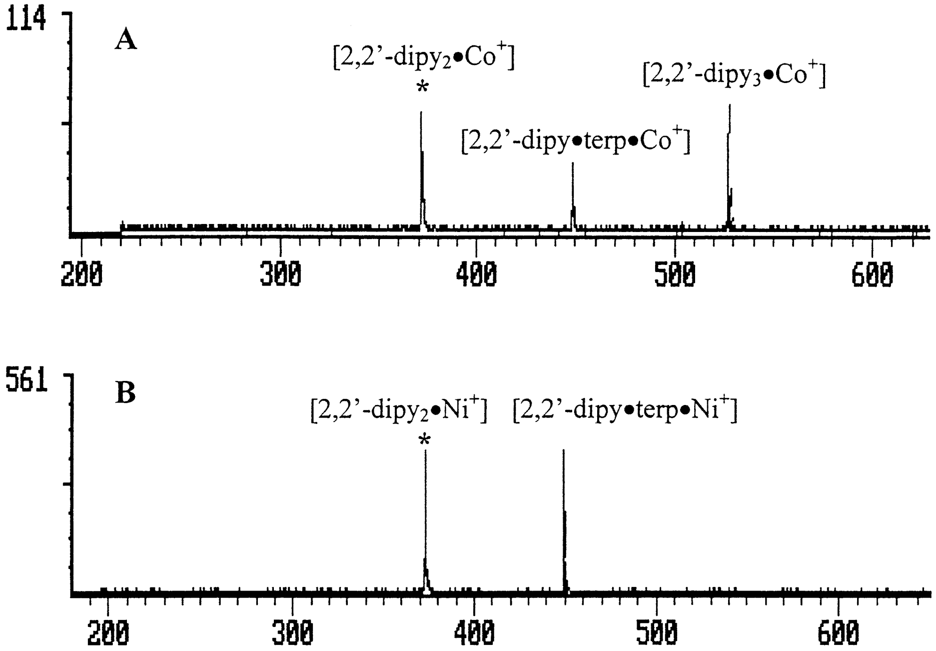

Fig. 3. Displacement of 2,2′-dipyridine by 2,2′:6,2″-terpyridine from **(A)** an isolated [2,2′-dipyridine$_2$ · Co$^+$] complex* after 50 ms or **(B)** an isolated [2,2′-dipyridine$_2$ · Ni$^+$] complex* after 200 ms.

because [2,2′-dipyridine$_3$ · Co$^+$] and [1,10-phenanthroline$_3$ · Co$^+$] complexes are stable species, suggesting indirectly that the Co$^+$ ion can accommodate up to six coordination sites and implying that two pyridine molecules could coexist with one or even two bidentate pyridyl ligands around the metal ion. Two explanations may contribute to the absence of such complexes. First, the bidentate ligands may have such significantly greater binding free energies than pyridine that they rapidly displace the remaining pyridine ligands, thus preventing the survival and detection of the intermediate [pyridine · L2$_2$ · Co$^+$] or [pyridine$_2$ · L2 · Co$^+$] complexes on the timescale of the experiment. In fact, the energy of association for a bidentate L2 to join an existing dimer complex may be greater than the binding energy of one or both pyridine ligands involved in the complex. Thus, in the collision complex, the more weakly bound pyridine would be displaced and the more strongly bound L2 would fully associate with the metal ion. A second possibility is that the two pyridine molecules initially coordinated to the metal ion may naturally bind in a linear fashion to minimize their repulsions; thus, the approach and attachment of a bidentate pyridyl molecule may unilaterally dislodge one of the pyridine molecules and prevent the survival of the [pyridine$_2$ · L2 · Co$^+$] species.

Reactions of the [pyridine$_2$ · Ni$^+$] complexes lead to a similar array of products, as shown in Table 1, second group of entries. Based on our previous study, Ni$^+$ can be coordinated by up to three monodentate pyridyl ligands, two bidentate pyridyl ligands, or two tridentate ligands [11]. The formation of mixed-ligand dimer complexes is observed upon reaction of each pyridyl ligand (L2) with [pyridine$_2$ · Ni$^+$], but again mixed-ligand trimer complexes are not observed except for the reactions with 4,4′-dipyridine. Upon reactions with 4,4′-dipyridine, both [pyridine$_2$ · 4,4′-dipyridine · Ni$^+$] and [pyridine · 4,4′-dipyridine$_2$ · Ni$^+$] are observed, confirming that these monodentate pyridyl ligands have similar coordination strengths and thus both can compete for binding the Ni$^+$ ion. Reactions of the [pyridine$_3$ · Ni$^+$] complexes reflect some subtle differences. First, the mixed-ligand trimer

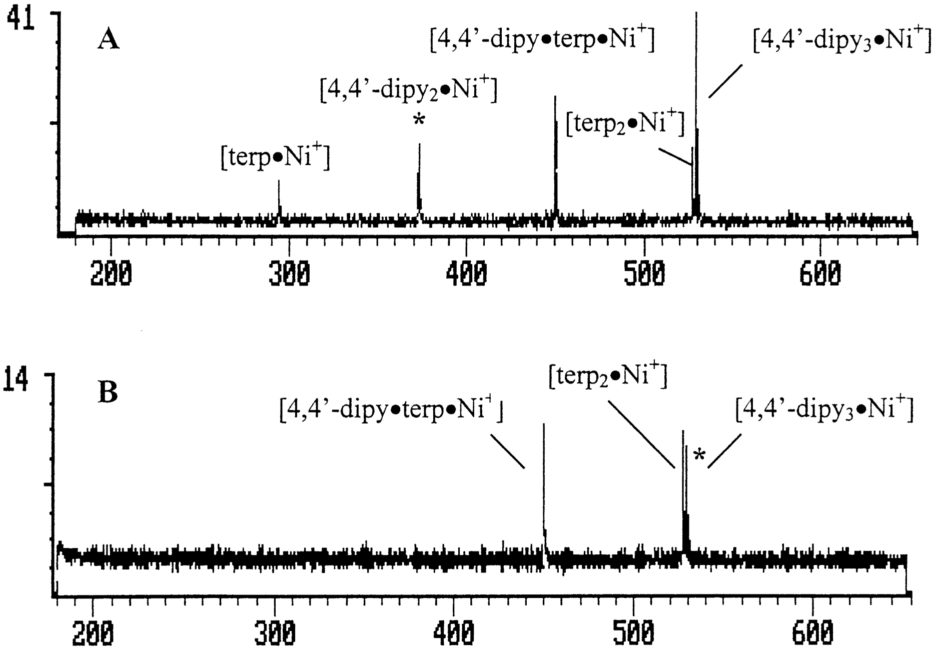

Fig. 4. Displacement of 4,4′-dipyridine by 2,2′:6,2″-terpyridine from **(A)** an isolated [4,4′-dipyridine$_2$ · Ni$^+$] complex after 100 ms or **(B)** an isolated [4,4′-dipyridine$_3$ · Ni$^+$] complex after 400 ms.

species, [pyridine$_2$ · L2 · Ni$^+$] is observed upon reactions with 2,2′-dipyridine but not 1,10-phenanthroline. The formation of the [pyridine$_2$ · 2,2′-dipyridine · Ni$^+$] trimers suggests that the presence of three pyridine ligands around Ni$^+$ shields the metal ion sufficiently well and delocalizes the positive charge such that the subsequent displacement reactions with 2,2′-dipyridine are slower than the analogous reactions between 2,2′-dipyridine and the [pyridine$_2$ · Ni$^+$] complexes. Thus, the mixed-ligand [pyridine$_2$ · 2,2′-dipyridine · Ni$^+$] intermediates survive on the timescale of the experiment. These intermediates were not observed upon the reactions of 1,10-phenanthroline and [pyridine$_3$ · Ni$^+$] because the coordination strength of 1,10-phenanthroline is greater than that of 2,2′-dipyridine, making the displacement reactions more exoergic.

Cu$^+$ can be coordinated by up to two monodentate, bidentate or tridentate ligands, as mentioned above [11]. The displacement reactions involving [pyridine$_2$ · Cu$^+$] and any of the other pyridyl ligands (L2) offer no surprises (see Table 1, last group of entries). In each case, stable mixed-ligand dimers are observed along with favorable formation of the [L2$_2$ · Cu$^+$] complexes. The mixed-ligand dimers are substantially less dominant upon the reactions with terpyridine (Fig. 2) because of the much greater coordination strength of terpyridine which causes rapid displacement of both pyridine molecules and allows survival of only a few of the mixed-ligand complexes.

One interesting trend to note is that if stable trimers, [L2$_3$ · M$^+$], can form with the metal and the displacing ligand, they will with one exception, [4,4′-dipyridine$_3$ · Ni$^+$]. There are two reasons for this trend. First, the effective coordination of a metal ion correlates with its stability. In most cases the trimer species offer a greater degree of coordination for the metal and, thus, would be more stable and appear preferentially to the dimer species. For example, three 2,2′-dipyridine ligands can coordinate one cobalt ion at up to six sites. On the other hand, the dimer complex of pyridine and cobalt, [pyridine$_2$ · Co$^+$], would have cobalt coordinated at a maximum of two sites. Clearly the trimer of 2,2′-dipyridine would incorporate a more fully coordinated and thus more stable metal ion than a dimer of pyridine, and over time the trimer product appears as the dominant product. Second, the larger ligands are more polarizable and better able to stabilize positive charges than the smaller pyridine. Therefore one would expect for the same degree of coordination of a metal that the larger ligand complexes would be more stable (barring any steric strain or hindrances). This is evidenced by the ability of 4,4′-dipyridine to displace pyridine from both the dimer and trimer complexes. Metal ions involved in a dimer complex with either 4,4′-dipyridine or pyridine would be coordinated at a maximum of two sites. The larger size of 4,4′-dipyridine enhances the stability of its dimers relative to that of pyridine. The one exception where exchanged ligand trimers do not form is when 4,4′-dipyridine reacts with the [pyridine$_3$ · Ni$^+$] trimers. However, mixed-ligand trimers do appear as [pyridine$_2$ · 4,4′-dipyridine · Ni$^+$] and [pyridine · 4,4′-dipyridine$_2$ · Ni$^+$] after 800 ms. This may be a case where the displacement of pyridine by the other monodentate ligand, 4,4′-dipyridine, is slow enough that all three pyridine ligands cannot be displaced on the timescale of the experiment.

The appearance of mixed-ligand dimers is always important and indicative of step-wise formation of the final exchanged dimers. They appear in all cases except one. When 4,4′-dipyridine displaces pyridine from [pyridine$_3$ · Ni$^+$] complexes, no dimers incorporating both pyridine and 4,4′-dipyridine are seen. Since 4,4′-dipyridine cannot chelate the metal, it is thermodynamically unfavorable to go from a three ligand (tricoordinate) metal complex to a bicoordinate complex. Rather a displacement of one pyridine at a time occurs, and the formation of mixed-ligand trimers results.

Finally, when terpyridine is the displacing ligand, it can displace pyridine from the various [pyridine$_2$ · M$^+$] complexes to form [terpyridine · M$^+$] complexes. Because terpyridine is a tridentate ligand, the [terpyridine · M$^+$] complex may have the metal ion coordinated at three sites, resulting in a more stable complex than [pyridine$_2$ · M$^+$].

3.3. Displacement of 2,2′-dipyridine

The displacement reactions of the 2,2′-dipyridine/metal complexes are summarized in Table 2. 2,2′-Dipyridine is a larger, bidentate molecule with two rings that can effectively chelate metal ions. Ni$^+$ and Cu$^+$ can coordinate up to two 2,2′-dipyridine ligands, while Co$^+$ can complex up to three [11]. The displacement of this chelating ligand from dimer and trimer metal complexes by larger bi- and tridentate ligands is of interest to compare to the displacement of nonchelating ligands, especially 4,4′-dipyridine (as described in Sec. 3.4.).

Examples of the displacement reactions involving 2,2′-dipyridine complexes are shown in Fig. 3. In Fig. 3(A), the reactions of [2,2′-dipyridine$_2$ · Co$^+$] with terpyridine are shown, and the reactions of [2,2′-dipyridine$_2$ · Ni$^+$] with terpyridine are shown in Fig. 3(B). Terpyridine can displace only one of the 2,2′-dipyridine ligands from [2,2′-dipyridine$_2$ · M$^+$] dimer complexes with either Co$^+$ or Ni$^+$. Conversely, the smaller, weaker 1,10-phenanthroline is able to displace both 2,2′-dipyridine ligands. These results indicate that a second terpyridine ligand is unable to approach and dislodge the remaining 2,2′-dipyridine ligand because of ligand repulsions and shielding of the metal ion, while the less sterically hindered 1,10-phenanthroline can orient itself such that a lower energy dimer complex can form.

Upon reaction of the [2,2′-dipyridine$_2$ · Co$^+$] complexes with 1,10-phenanthroline, the displacement of one or both 2,2′-dipyridine ligands is the dominant process, resulting in stable mixed-ligand dimers and [1,10-phenanthroline$_2$ · Co$^+$] dimers. The two possible types of mixed-ligand trimers, [2,2′-dipyridine$_2$ · 1,10-phenanthroline · Co$^+$] and [2,2′-dipyridine · 1,10-phenanthroline$_2$ · Co$^+$] are also observed, indicating that the displacement reactions occur in a step-wise fashion for these two ligands and that the coordination strengths of these two bidentate ligands are reasonably similar to allow competitive survival of the two types of trimer complexes.

The displacement reactions of the [2,2′-dipyridine$_3$ · Co$^+$] complexes are especially interesting because these complexes represent a case where the metal ion is already fully coordinated. Reactions with 1,10-phenanthroline indicate a slow step-wise displacement of one, then two, then all three 2,2′-dipyridine ligands, resulting in the sequence of products [2,2′-dipyridine$_2$ · 1,10-phenanthroline · Co$^+$], [2,2′-dipyridine · 1,10-phenanthroline$_2$ · Co$^+$], and [1,10-phenanthroline$_3$ · Co$^+$]. The reactions with terpyridine are strikingly different. Instead of rapid displacement of the 2,2′-dipyridine ligands, the displacement reactions are nearly quenched. In fact, no products corresponding to displacement of just one 2,2′-dipyridine molecule are observed (i.e. formation of [2,2′-dipyridine$_2$ · terpyridine · Co$^+$]) and only a minor amount of products corresponding to displacement of two 2,2′-dipyridine ligands are observed (i.e. formation of [2,2′-dipyridine · terpyridine · Co$^+$]). This initially odd result stems from the fact that when terpyridine attempts to displace a single 2,2′-dipyridine ligand, the resulting intermediate does not easily allow all three donor atoms of terpyridine to coordinate the metal ion because the maximum coordination number of Co$^+$ would be exceeded. Thus, terpyridine must displace *two* 2,2′-dipyridine molecules simultaneously to allow formation of a stable complex, which is clearly a slow and statistically unfavored process.

The displacement reactions of [2,2′-dipyridine$_2$ · Cu$^+$] are straightforward. In each case, 1,10-phenanthroline or terpyridine may displace one or both 2,2′-dipyridine ligands, and trimer species are not formed for these metal ions. Interestingly, when terpyridine interacts with [2,2′-dipyridine$_2$ · Cu$^+$], both mixed-ligand dimers and terpyridine dimers are observed, as is the case with phenanthroline. The d^{10} electronic configuration of Cu$^+$ may play an important role in the ability of terpyridine to form stable terpyridine dimer complexes with it and not with Co$^+$ (d^8) or Ni$^+$ (d^9).

3.4. Displacement of 4,4′-dipyridine

4,4′-dipyridine is an isomer of 2,2′-dipyridine with the important distinction that it cannot chelate a metal ion because of the unfavorable positions of its two nitrogen atoms. This compound should serve as a useful reference to compare how larger ligands displace it versus displacing a smaller nonchelator such as pyridine or a similar sized chelator such as 2,2′-dipyridine. The results are summarized in Table 3. In general, the displacement reactions clearly illustrate that the coordination strength of 4,4′-dipyridine is lower than that of 2,2′-dipyridine because the displacement reactions are generally more efficient than the ones described in Table 2. For example, for all of the [4,4′-dipyridine$_2$ · M$^+$] complexes, 1,10-phenanthroline and terpyridine can displace both of the 4,4′-dipyridine ligands. For the [4,4′-dipyridine$_3$ · Ni$^+$] complex, displacement of two 4,4′-dipyridine ligands occurs so rapidly that the intermediate [4,4′-dipyridine$_2$ · 1,10-phenanthroline · Ni$^+$] complex is never observed. Interestingly, no mixed-ligand trimer species are observed when phenanthroline displaces 4,4′-dipyridine from [4,4′-dipyridine$_2$ · Co$^+$], while they were observed for the analogous reactions of [2,2′-dipyridine$_2$ · Co$^+$] (Table 2). Because each 4,4′-dipyridine (or pyridine) ligand reacts with the metal at only one site, it is easier for the larger phenanthroline ligand to not only approach and bind to the complex at two sites, but in so doing displace the monodentate ligand and prevent the survival of the trimer intermediate.

Monomer complexes, [terpyridine · M$^+$], were observed as products when terpyridine displaced 4,4′-dipyridine from [4,4′-dipyridine$_2$ · M$^+$] complexes with nickel and copper. Again, this result parallels that seen with pyridine, while no [terpyridine · M$^+$] complexes were ever observed in the analogous 2,2′-dipyridine experiments. However, when the isolated initial complex was a trimer, as with [4,4′-dipyridine$_3$ · Ni$^+$], no monomer species were produced. These results are illustrated for terpyridine reacting with [4,4′-dipyridine$_2$ · Ni$^+$] and [4,4′-dipyridine$_3$ · Ni$^+$] complexes in Figs. 4(A) and 4(B), respectively. The [terpyridine · Ni$^+$] complex is clearly present as a product after 100 ms reaction time with [4,4′-dipyridine$_2$ · Ni$^+$], even though more fully coordinated Ni$^+$ species, such as [4,4′-dipyridine · terpyridine · Ni$^+$] and [4,4′-dipyridine$_3$ · Ni$^+$], are present in greater abundance. The absence of [terpyridine · Ni$^+$] complexes in Fig. 4(B) indicates that terpyridine cannot displace all three 4,4′-dipyridine molecules.

The main factors that mediate this behavior appear to be the tridentate nature of terpyridine and the type of initial complex (dimer or trimer). A metal ion coordinated with a single tridentate ligand is more fully coordinated and more stable than a metal ion coordinated with two monodentate ligands; thus, terpyridine may be able to displace not just one but two 4,4′-dipyridine ligands and produce a more stable [terpyridine $\cdot$ M^+] complex. However, even though terpyridine is tridentate, it cannot competitively coordinate a metal ion already attached to three ligands regardless of whether they are chelators or not. The mixed-ligand dimer product observed when terpyridine displaces 4,4′-dipyridine from [4,4′-dipyridine$_3$ $\cdot$ Ni^+] indicates at most two ligands can be removed while one terpyridine adds to the metal. This may be because the limited flexibility terpyridine has to orient its three donor nitrogen atoms toward the metal cation relative to the three independent monodentate 4,4′-dipyridine ligands. This idea is supported by work done by Armentrout and co-workers involving lithium cation-polyether complexes [22,23]. It was found that the orientation of the C–O–C subunits in the polyethers was a main factor in determining the stability of the complexes. Thus multidentate ligands such as 12-crown-4 and 1,2-dimethoxyethane had lower bond dissociation energies when complexed with lithium as compared to two or four monodentate dimethyl ether ligands in analogous complexes because the multidentate ligands could not orient their oxygen atoms toward the cation as optimally as the independent dimethyl ether molecules [22,23].

4. Conclusions

Ligand exchange reactions in the gas-phase allowed systematic study of the factors governing ligand displacement and metal binding interactions, in particular when the metal ions were already fully coordinated and the charge was highly delocalized. The model complexes in this study underwent stepwise ligand displacement reactions that were clearly mediated by the size of the ligand which affected its ability to delocalize the charge and most importantly the chelating ability of the ligand which influenced its binding free energy. Based on the reactions of the dimer and trimer metal complexes, the order of binding free energies followed the trend: pyridine $<$ 4,4′-dipyridine $<$ 1,10-phenanthroline $<$ 2,2′:6′,2″-terpyridine, which agreed with the order found in previous studies [11,12]. The small, nonchelating pyridine was obviously the weakest ligand because it was readily displaced from all metal complexes by each of the other ligands. 4,4′-Dipyridine was a stronger ligand in the gas phase because of its greater size and, thus, ability to stabilize the positively charged metal ion. 2,2′-Dipyridine, the chelating isomer of 4,4′-dipyridine, was stronger than either of the two monodentate ligands and underwent dramatically different displacement reactions resulting in far fewer completely exchanged products. Bidentate 1,10-phenanthroline and tridentate 2,2′:6′,2″-terpyridine demonstrated the highest binding free energies, although steric effects allowed the smaller 1,10-phenanthroline to undergo more efficient exchange reactions than the bulkier terpyridine, as observed upon reactions with the [2,2′-dipyridine$_2$ $\cdot$ Ni^+], [2,2′-dipyridine$_2$ $\cdot$ Co^+], or [2,2′-dipyridine$_3$ $\cdot$ Co^+], complexes.

Ligands with chelating abilities frequently displaced two nonchelating ligands so rapidly that the observation of stable mixed-ligand complexes on the timescale of the experiment was prohibited. The rates of the displacement reactions, as reflected in the product distributions, generally correlated with the relative binding free energies of the ligands, with the exception of some cases in which the metal ion was initially fully coordinated by two or three chelating ligands. In these latter cases, the displacement reactions were severely slowed or even quenched, presumably because of the blocking of the approach and orientation of the incoming ligand, thus, reducing its effective coordination ability. Understanding these factors in simple model systems gives some insight into the coordination chemistry occurring in larger more complex systems found in other areas of chemistry and biochemistry.

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