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The utility of ion–molecule reactions in a quadrupole ion trap mass spectrometer for analyzing metal complex coordination structure

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Abstract

Gas-phase ion–molecule reactions of metal complex ions with acetonitrile in a quadrupole ion trap mass spectrometer are shown to have some potential for determining the number and types of functional groups bound to a metal. Metal complexes with varying coordination spheres show significant differences in their gas-phase reactivity with acetonitrile. The relative product ion intensities observed in the mass spectrum after a given reaction time provide the appropriate data to distinguish complexes with different coordination spheres. Experimental parameters suspected to have an effect on the reproducibility of these intensities are examined in order to understand better which factors need to be most closely controlled to maximize precision. Ni(II) and Cu(II) complex ions of the pentadentate ligands 1,9-bis(2-imidazolyl)-2,5,8-triazanonane (DIEN-$(imi)_2$) and 1,9-bis(2-tetrahydrofuranyl)-2,5,8-triazanonane (DIEN-$(THF)_2$) are reacted in the gas-phase at different temperatures, pressures of acetonitrile, and pressures of buffer gas (helium) in a modified quadrupole ion trap mass spectrometer. The effects of such experimental variations on the product ion intensities are measured and analyzed. Under conditions where the precision is maximized, the temperature and acetonitrile pressure seem to have the biggest impact on the reproducibility of the resulting product ion intensity with the acetonitrile level being slightly more important. The reproducibility of ion intensities for the reactions of the Ni(II) complexes are the lowest due to their higher reactivity, while the measurements for the Cu(II) complexes have a higher degree of precision. In general, with careful control of the temperature and reagent gas pressure, ion–molecule (I–M) reactions seem to be a promising method for providing a rapid and sensitive analysis of the functional groups bound to a metal in a given complex.
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Keywords: Ion–molecule reactions; Transition metal complexes; Coordination structure; Quadrupole ion trap mass spectrometry

1. Introduction

Mass spectrometry (MS) has long been known as a very sensitive analytical technique. Recent application to the analysis of peptides and proteins has highlighted its remarkable structural elucidation potential. This powerful combination of sensitivity and structural analysis capability is having a profound impact on proteomic research. These benefits, however, are not just limited to biochemical analyses.

We have recently become interested in using MS to obtain structural information for metal complexes present at trace levels in marine environments. In particular, we are interested in using MS to determine

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the type, number, and orientation of the ligand(s) (i.e. coordination structure) around a metal. The chemical nature and orientation of the functional groups bound to a metal very much influence the redox potentials, magnetic properties, catalytic activity, lability, binding ability, and general reactivity of the metal center. Simply put, knowledge of a metal's coordination structure is critical for understanding its chemistry. MS may offer a means of overcoming some of the drawbacks to traditional techniques used to study metal complex coordination structure. Techniques such as NMR spectroscopy, X-ray crystallography, electrochemistry, Raman spectroscopy and extended X-ray absorption fine structure (EXAFS) have been successfully used to establish coordination structure for metal complexes. These methods, however, are generally either not sensitive enough to provide information at trace levels or have difficulty when analytes are present in a mixture like those of interest in marine waters.

Upon the development of ionization techniques like electrospray ionization (ESI), MS has become more useful for studying metal complexes in environmentally and biologically relevant oxidation states. As with the analysis of peptide and proteins, tandem MS (MS/MS) is typically used in conjunction with collision-induced dissociation (CID) to provide structural information for metal complexes. Detailed coordination structure from CID, though, is not something that can be easily gathered, partly because the dissociation chemistry of transition metal–ligand complexes has received relatively little attention. Brodbelt and co-workers have studied the dissociation patterns of polyether, crown ether, and polypyridyl complexes of singly charged [1,2] and doubly charged transition metal ions [3,4]. Details about the effect of ligand flexibility and metal type on dissociation pathways has been gathered from these studies. Other work has also applied CID to transition metal complexes [5–8]. In general, these studies reveal that rearrangement reactions involving the loss of small neutrals from large ligands or the loss of intact ligands from multi-ligated metal ions are typical. Unfortunately, neither provides much insight into the coordination sphere because they do not reveal whether the groups lost were coordinated to the metal or not. Some evidence of the utility of CID to provide coordination structure of metal complexes can be seen in the investigations of transition metal–peptide complexes [9–16]. In complexes containing cysteine and histidine the preferred dissociation pathways are ones along the peptide backbone adjacent to the coordinating side chain [10–12,15]. While in these cases correlations between gas-phase binding and solution-phase binding of transition metal–peptide complexes could be inferred from the CID spectra, very little evidence was presented to suggest coordination sphere structure could be determined a priori. Elucidation of metal–ligand connectivity using CID alone seems to be limited ultimately by the inability to determine whether a fragment lost during CID was initially coordinated to the metal or not. Also, the activating nature of CID and the inherent weakness of some metal–ligand interactions may obscure the precise information that is desired.

Thus, we have begun to investigate the possibility of using ion–molecule (I–M) reactions as an alternative to CID. I–M reactions involve reacting the analyte ion of interest in the gas-phase with specific neutral reagents. The resulting product ions then provide some chemical information about the initial parent ion. I–M reactions have been effectively used to provide structural information often not accessible by CID [17–26], and the analytical utility of I–M reactions has been reviewed recently [17,18]. Due to the inherent gentleness of I–M reactions, useful insight into the coordination structure of metal complexes might be gathered. I–M reaction studies of metal complexes are abundant, but these studies have been limited mostly to ions in low oxidation states with the goal of better understanding catalytic processes in which metals are involved [27,28]. Recently, several studies have used I–M reactions as probes for obtaining structural information of metal complexes [29–36]. For example, the possibility of gathering coordination number information from the reactions of model metal complexes with reagent ligands such as pyridine, ammonia, water and methanol was investigated [30]. Another study of metal complexes with ion pairs showed that I–M reactions can distinguish inner- and outer-sphere ligands as well as the coordination modes of some counterions [31]. The combination of I–M reactions and CID to investigate metal complex structure has been also explored [32]. More recent studies indicate that the gas-phase reactivity of transition metal complexes with a given reagent gas is highly dependent upon the functional groups in the coordination sphere [35] and the metal center [36].

In this work we further extend the idea that I–M reactions might be useful for providing metal coordination structure. Specifically, I–M reactions may have utility for providing the number and types of functional groups around a metal center in an unknown complex. If indeed I–M reactions are to be analytically useful in this manner, a detailed analysis of the experimental factors that affect such reactions is essential. An understanding of the effect of such factors on complex reactivity will ensure that these parameters are controlled so that differences observed can be related to meaningful chemical information. In this study we investigate several factors that are likely to affect the observed reactivity of metal complexes in order to understand the degree to which they are likely to affect the precision and accuracy of any analytical information that is gathered.

2. Experimental

Gas-phase I–M reactions are performed in a quadrupole ion trap mass spectrometer (Bruker ESQUIRE-LC, Billerica, MA) adapted to introduce small quantities of a reagent gas through a leaking system that replaces the He inlet in the original instrument. Two precision leak valves (MDC Vacuum Products Corporation, Hayward, CA) control the admission of the reagent gas and helium to the vacuum system, and a third valve is used to leak ammonia (99.99%, Matheson Tri-gas, Parsippany, NJ) into the system, which is used to calibrate the pressure. Acetonitrile (99.5%, Aldrich) is placed in a small glass ampoule connected to one of the precision leak valves, and several freeze/pump/thaw cycles are performed to evacuate non-condensable gases in the liquid. A capacitance manometer (Kurt J. Lesker Company, Clairton, PA) is used as a reference to monitor the acetonitrile and helium pressure in the valve system and to ensure reproducible introduction of the gas into the analyzer region. The pressure inside the quadrupole ion trap is monitored using an ion gauge. The reading provided by the ion gauge is calibrated using the reported deprotonation reaction rates of the 13^+, 12^+ and 11^+ charge states of ubiquitin with ammonia [37]. A correction factor is derived and used to obtain the true gas pressure from the ion gauge reading. Different helium buffer gas pressures of $(4.7 \pm 0.6) \times 10^{-3}$ Pa, $(8.3 \pm 0.8) \times 10^{-3}$ and $(1.29 \pm 0.02) \times 10^{-2}$ Pa and acetonitrile pressures of $(2.0 \pm 0.4) \times 10^{-5}$ Pa, $(2.8 \pm 0.4) \times 10^{-5}$ Pa and $(3.9 \pm 0.4) \times 10^{-5}$ Pa are used. In a series of experiments, the vacuum system temperature is adjusted and maintained at 301, 303, and 305 ± 1 K with a heating blanket. The actual temperature inside the volume of the quadrupole ion trap electrodes is unknown. Instead the temperature of the vacuum chamber walls is measured using a thermocouple to get a rough estimate of the temperature inside the mass spectrometer.

The ligands used in these experiments are shown in Fig. 1 and were synthesized by formation and reduction of a Schiff base. A detailed description of the synthetic conditions for each ligand has been reported previously [35]. Metal complexes are prepared by mixing equimolar amounts of $NiCl_2$ or $CuCl_2$ and the ligands of interest in methanol or water:methanol (1:1). Complex ions are transferred to the gas-phase by ESI using a needle voltage of 3.5–4.0 kV and a flow rate of 1.0–2.0 μl/min. Typically, a capillary temperature of 200 °C and a capillary exit offset voltage of 20 V are used. Once in the ion trap, the metal complex ions of interest are isolated and reacted with acetonitrile for different periods of time. The ion isolation process and the reaction time are controlled using the ESQUIRE-LC software. The quadrupole ion trap scan function used by the ESQUIRE-LC software contains several fixed scan delays between ion isolation and acquisition that cannot be changed by the user. Consequently, the shortest reaction time accessible is 10.5 ms. Kinetic data are obtained by monitoring the intensity of the parent and product ions over times ranging from 10.5 to 4000 ms. The reactions follow the general form depicted in Eq. (1):

$$\mathrm{ML}^{2+} + \mathrm{CH_3CN} \underset{k_2}{\overset{k_1}{\rightleftarrows}} (\mathrm{ML} + \mathrm{CH_3CN})^{2+} \underset{k_4}{\overset{k_3}{\rightleftarrows}} (\mathrm{ML} + 2(\mathrm{CH_3CN}))^{2+} \quad (1)$$

Equilibrium constants are calculated as a ratio of rate constants (k_1/k_2), which are determined by fitting the experimental data to a series of differential equations using the KinFit program [38]. In some cases, where the KinFit program fails to provide meaningful rate constants, the equilibrium constant is evaluated as the

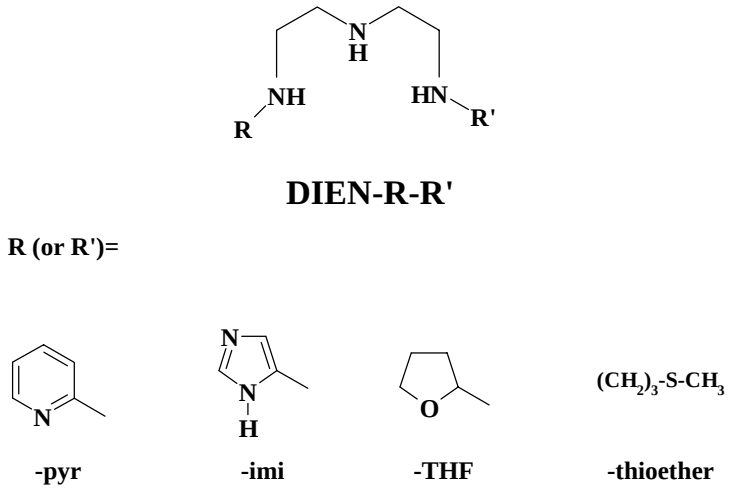

Fig. 1. Structures of the ligands used in this study.

ratio of the product/parent ion intensities from the mass spectrum.

3. Results

In a previous study we demonstrated that the reactivity of Co(II) and Cu(II) complexes depended strongly on the types of functional groups in the coordination sphere [35]. Fig. 2 shows a plot of the parent and product ion intensities for the reaction of $Co(DIEN\text{-}(imi)_2)^{2+}$ with acetonitrile over time. From this data forward and back reaction rate constants as well as an equilibrium constant can be determined. Table 1 shows the forward reaction rate constants and equilibrium constants for several Co(II) complexes. Clearly the rate and equilibrium constants are different depending upon the ligand that is bound to the metal. Because having different functional groups in the coordination sphere of a metal clearly affects the reactivity of its complexes, I–M reactions might be useful for identifying the functional groups attached to a metal whose coordination structure is unknown.

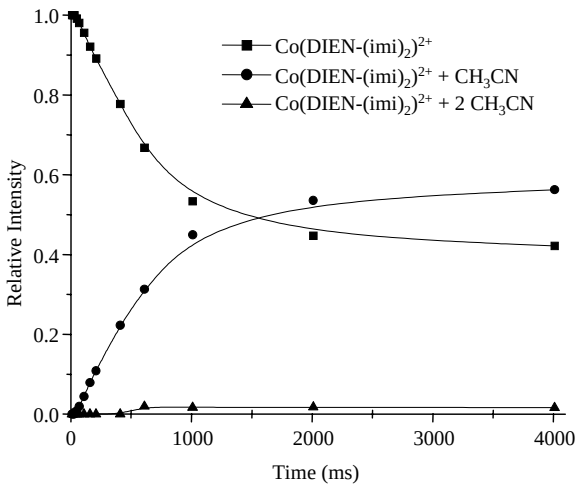

Fig. 2. Kinetic plot for the association reaction of acetonitrile with $Co(DIEN\text{-}(imi)_2)^{2+}$.

Because we are interested in the potential analytical utility of these I–M reactions, we have attempted to identify simple experimental conditions that would allow us to determine the number and types of the functional groups in the coordination sphere of a metal complex. Ideally this would require obtaining a single mass spectrum at a short reaction time in order to maximize the speed of the measurement. Table 1 shows that a majority of the equilibrium constants for the given complexes are statistically different. This means that the mass spectra resulting from the reaction of these complexes for sufficient time to establish an equilibrium should be noticeably different. For all our reactions, however, an equilibrium was not established until after 500 ms, and in most cases ∼1000 ms is required to reach an equilibrium.

Table 1
Rate and equilibrium constants for the addition of acetonitrile to selected Co(II) complexes

Ligand	Rate constants (10^{-10} cm^3 per molecule s^{-1})[a]	Equilibrium constants[b]
DIEN-$(THF)_2$	6 ± 1	220 ± 60
DIEN-(THF)(thioether)	4.1 ± 0.6	130 ± 25
DIEN-$(thioether)_2$	3.5 ± 0.4	75 ± 30
DIEN-(THF)(pyr)	3 ± 1	65 ± 20
DIEN-(THF)(imi)	2.8 ± 0.1	10 ± 2
DIEN-$(pyr)_2$	2.3 ± 0.4	4.7 ± 0.3
DIEN-(thioether)(pyr)	1.7 ± 0.2	3 ± 1
DIEN-$(imi)_2$	1.0 ± 0.3	1.4 ± 0.2
DIEN-(thioether)(imi)	0.8 ± 0.2	1.2 ± 0.1

[a] These values were obtained by fitting Eq. (1) to the experimental data.
[b] The equilibrium constants were determined from the following equation: $K = k_1/k_2$, where k_1 and k_2 are found by fitting the experimental data to Eq. (1).

Because a shorter reaction period is preferred, an alternative was considered. Most of the reaction rate constants listed for the complexes in Table 1 are also statistically different, and these values are indicative of the reaction dynamics up to the establishment of the equilibrium. Therefore, obtaining a mass spectrum at shorter reaction times should also provide readily distinguishable data. The spectra that result from a 110 ms reaction of acetonitrile with Co(DIEN-$(imi)_2)^{2+}$, Co(DIEN-$(thioether)_2)^{2+}$, and Co(DIEN-$(THF)_2)^{2+}$ are shown in Fig. 3. A reaction time of 110 ms was chosen because it represents a point in the reaction where the intensities of the parent and product ions are changing rapidly. Fig. 3 clearly shows that different spectra result. Also indicated in Fig. 3 are the reaction rate constants that were determined for the given complexes during the conditions shown. Clearly, even complexes with similar reaction rate constants have noticeably different spectra. The relative intensities of the product ions in Fig. 3 are 10, 40 and 55% for the reactions of Co(DIEN-$(imi)_2)^{2+}$, Co(DIEN-$(thioether)_2)^{2+}$, and Co(DIEN-$(THF)_2)^{2+}$, respectively.

The parent and product ion intensities after a 110 ms reaction time for the complexes shown in Table 1 are listed in Table 2. This table shows that while carefully controlling the experimental conditions, normal random fluctuations in parent ion intensities result in relative standard deviations ranging from 2 to 22%. The data in Table 2 shows that the product and parent ion intensities are noticeably different for many of the complexes within the precision of the measurement.

For comparison Fig. 4 shows the spectra that result when the same three complexes are allowed to react until an equilibrium is surely established (2010 ms). Like in Fig. 3 these spectra are clearly different for each complex. In contrast to Fig. 3, the I–M reaction spectra of these complexes show a small addition of a second acetonitrile molecule. Nonetheless, the differences in the product ion intensities again suggest that such spectra could be used to distinguish the coordination spheres of different metal complexes. Table 3 shows the parent and product ion intensities of each complex after a 2010 ms reaction with acetonitrile. In these cases the relative standard deviation of the product ion intensities (i.e. for the addition of one acetonitrile) range from 1 to 7%.

Table 2
Percentage of total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$) ions for the reactions of selected Co(II) complexes with acetonitrile for 110 ms (temperature: 300 ± 1 K; He pressure: (1.3 ± 0.4) × 10^{-2} Pa; acetonitrile pressure: (4.3 ± 0.4) × 10^{-5} Pa)

Ligand	ML^{2+}	$(ML + CH_3CN)^{2+}$
DIEN-$(THF)_2$	54 ± 12	46 ± 12
DIEN-(THF)(thioether)	68 ± 9	32 ± 9
DIEN-$(thioether)_2$	67 ± 9	32 ± 9
DIEN-(THF)(pyr)	79 ± 13	21 ± 13
DIEN-(THF)(imi)	81.4 ± 0.3	18.6 ± 0.3
DIEN-$(pyr)_2$	77 ± 10	23 ± 10
DIEN-(thioether)(pyr)	90 ± 2	10 ± 2
DIEN-$(imi)_2$	92 ± 3	8 ± 3
DIEN-(thioether)(imi)	95 ± 2	5 ± 2

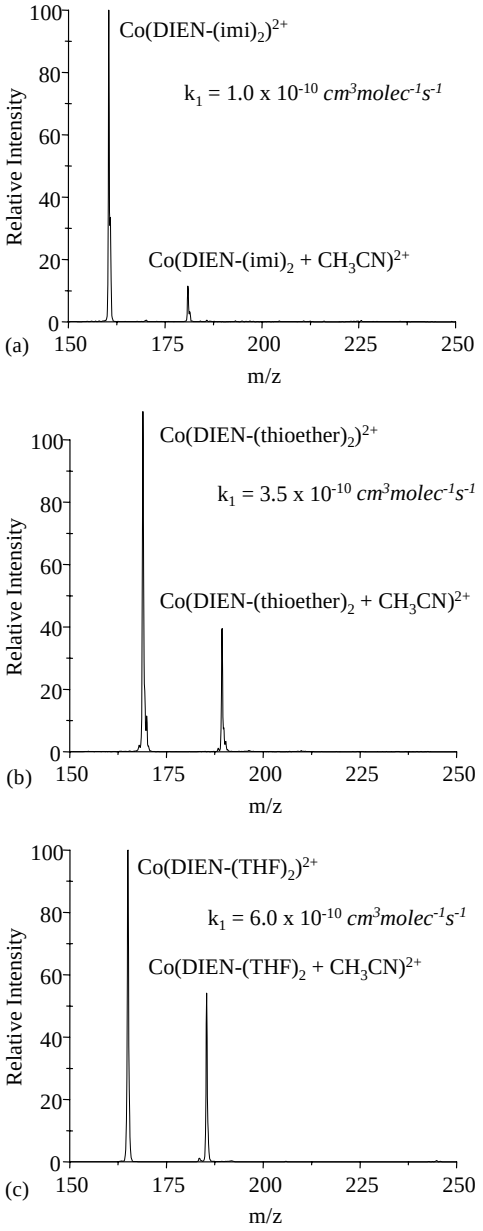

Fig. 3. Mass spectra for the 110 ms reaction of (a) DIEN-(imi)$_2$, (b) DIEN-(thioether)$_2$, and (c) DIEN-(THF)$_2$ complexes of Co(II) with acetonitrile.

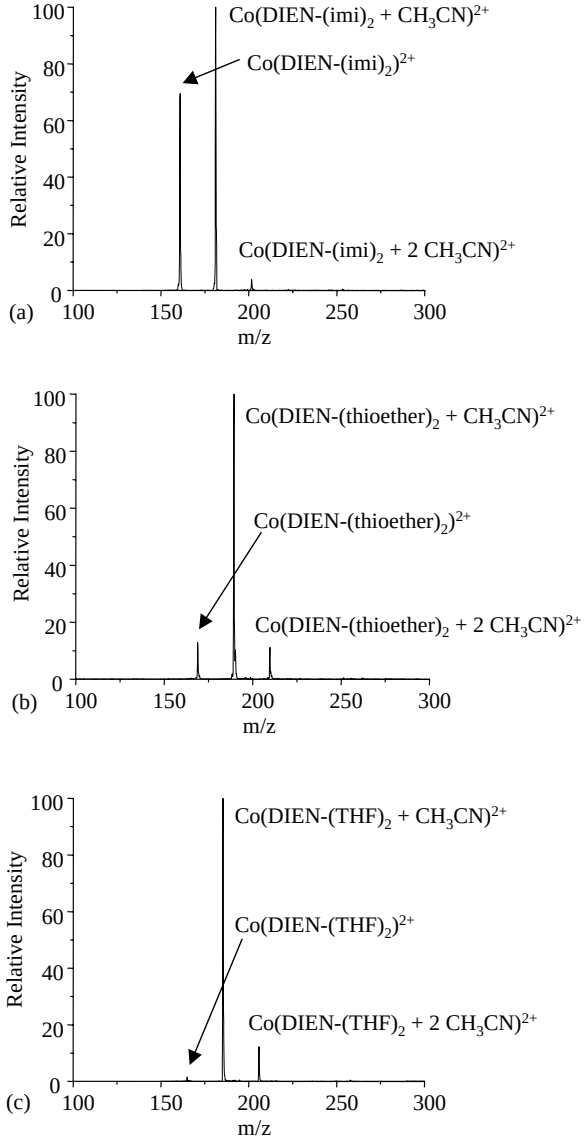

Fig. 4. Mass spectra for the 2010 ms reaction of (a) DIEN-(imi)$_2$, (b) DIEN-(thioether)$_2$, and (c) DIEN-(THF)$_2$ complexes of Co(II) with acetonitrile.

In general, the I–M reaction spectra of the various complexes shown in Table 1 and complexes of other metals (data not shown) [35,36] result in different spectra after a 110 ms reaction time and after an equilibrium is established. This means that performing I–M reactions on a metal complex might allow for the identification of the functional groups bound to the metal. To make this I–M reaction approach more routinely useful, two directions of research must be investigated.

First, an extensive collection of model complexes with a large variety of functional groups in the

Table 3
Percentage of total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$ and $(ML + 2CH_3CN)^{2+}$) ions for the reactions of selected Co(II) complexes with acetonitrile for 2010 ms (temperature: 300 ± 1 K; He pressure: $(1.3 \pm 0.4) \times 10^{-2}$ Pa; acetonitrile pressure: $(4.3 \pm 0.4) \times 10^{-5}$ Pa)

Ligand	ML^{2+}	$(ML + CH_3CN)^{2+}$	$(ML + 2CH_3CN)^{2+}$
DIEN-$(THF)_2$	1.2 ± 0.1	91 ± 3	8 ± 3
DIEN-(THF)(thioether)	1.7 ± 0.8	88 ± 4	10 ± 5
DIEN-$(thioether)_2$	8 ± 2	79 ± 2	12 ± 4
DIEN-(THF)(pyr)	5 ± 3	90.7 ± 0.8	4 ± 3
DIEN-(THF)(imi)	3.9 ± 0.5	91 ± 1	5 ± 1
DIEN-$(pyr)_2$	27 ± 6	72 ± 5	3.3 ± 0.2
DIEN-(thioether)(pyr)	16 ± 4	79 ± 3	5 ± 2
DIEN-$(imi)_2$	43 ± 2	54 ± 3	4 ± 2
DIEN-(thioether)(imi)	49 ± 3	50 ± 2	2.1 ± 0.1

coordination sphere of a given metal must be studied under well-controlled and defined conditions. From such a collection of model complexes, a database of I–M reaction data could be constructed. In this database, a metal, for example, that has two amine groups, two imidazole groups, and one thiol group bound to it would react to give certain ion intensities or rate and equilibrium constants. The general approach to determine the number and types of the functional groups in an unknown complex's coordination sphere would be to take the metal complex of interest, react it under the conditions used to collect the database, and compare the result to the collected database. A reasonable match in ion intensities, reaction rate constant, or equilibrium constant to an existing model complex in the database would then elucidate the functional groups bound to the metal in the unknown complex. Such an approach would be analogous to how coordination spheres are determined using EXAFS.

Second, the experimentally controllable factors that affect the I–M reactions—temperature, helium pressure and reagent gas pressure—would need to be studied to determine their effects on the reproducibility of the obtained spectra. *This second avenue of investigation is the subject of the remaining portion of this paper*.

The I–M reactions of acetonitrile with the metal complexes of interest are association reactions. Stabilization of the complex/acetonitrile gas-phase adduct occurs via collisions with a third body or by emission of radiation. In the quadrupole ion trap, the relatively high He pressures ($\sim 1 \times 10^{-2}$ Pa) likely make collisional stabilization the dominant cooling mechanism. Therefore, the following discussion will ignore radiative cooling. Only considering collisional stabilization, the association reaction takes the following general form (Eq. (2)):

$$ML^{n+} + R + He \underset{k_{diss}}{\overset{k_f}{\rightleftarrows}} (ML + R)^{n+} + He \quad (2)$$

where k_f is the rate constant for the formation of the adduct and k_{diss} is the rate constant for the reverse reaction. Three-body association reactions are generally accepted to involve two steps (Eqs. (3) and (4)):

$$ML^{n+} + R \underset{k_b}{\overset{k_a}{\rightleftarrows}} (ML + R)^{n+*} \quad (3)$$

$$(ML + R)^{n+*} + He \underset{k_{ac}}{\overset{k_s}{\rightleftarrows}} (ML + R)^{n+} + He \quad (4)$$

Clearly from these reactions, the amount of reagent gas and helium used are important for determining the extent of reaction. The kinetics and thermodynamics of these reactions are affected by temperature too. The normal variations observed in the product ion intensities shown in Tables 2 and 3 are likely caused by fluctuations in the helium pressure, reagent gas pressure, and/or temperature during the course of a single experiment or from 1 day to the next. In order to study which parameter has the largest impact on the measurements, so that extra effort can be taken to control it, we have carried out experiments to test the effect of each parameter on the reactivity of certain metal complexes. The helium pressures, acetonitrile pressures,

and temperatures used in these experiments were chosen to mimic the random fluctuations that could occur during an experimental procedure. The range of values chosen are very liberal estimates of the fluctuations that these factors could undergo during a set of experiments. In general, our experimental setup is able to control the helium and acetonitrile pressures within 5–15%, and the temperature can usually be controlled within ±1 K. In this study, we have varied the pressures over a range of 300% and varied the temperature over a 5 K range.

Metal complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ ligands were chosen because in previous studies they were found to exhibit a large range of reaction rates and equilibrium constants [35]. Ni(II) and Cu(II) were chosen as the metal centers in these complexes to maximize the range of fast and slow reacting complexes. Other work has shown that among the first-row divalent transition metals Ni(II) complexes in general are the most reactive, and Cu(II) complexes are the least reactive [30,36].

Table 4
Percentage of total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$ and $(ML + 2CH_3CN)^{2+}$) ions for the 110 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with varying pressures of acetonitrile (temperature: 301 ± 1 K; He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$
$(2.0 \pm 0.4) \times 10^{-5}$ Pa		
$Ni(DIEN\text{-}(imi)_2)^{2+}$	94 ± 1	6 ± 1
$Ni(DIEN\text{-}(THF)_2)^{2+}$	78 ± 13	22 ± 13
$Cu(DIEN\text{-}(imi)_2)^{2+}$	98.8 ± 0.1	1.2 ± 0.1
$Cu(DIEN\text{-}(THF)_2)^{2+}$	95.4 ± 0.3	4.6 ± 0.3
$(2.8 \pm 0.4) \times 10^{-5}$ Pa		
$Ni(DIEN\text{-}(imi)_2)^{2+}$	94 ± 2	6 ± 2
$Ni(DIEN\text{-}(THF)_2)^{2+}$	58 ± 8	42 ± 8
$Cu(DIEN\text{-}(imi)_2)^{2+}$	99 ± 1	1 ± 1
$Cu(DIEN\text{-}(THF)_2)^{2+}$	91.9 ± 0.9	8.1 ± 0.9
$(3.9 \pm 0.4) \times 10^{-5}$ Pa		
$Ni(DIEN\text{-}(imi)_2)^{2+}$	76 ± 1	24 ± 1
$Ni(DIEN\text{-}(THF)_2)^{2+}$	52 ± 13	48 ± 13
$Cu(DIEN\text{-}(imi)_2)^{2+}$	97 ± 1	3 ± 1
$Cu(DIEN\text{-}(THF)_2)^{2+}$	85 ± 2	15 ± 2

3.1. Effect of reagent gas pressure on product ion intensities

The amount of reagent gas used should have a direct effect on both the reaction rates and the equilibrium constants. In these experiments acetonitrile is used as the reagent gas. Under normal operating conditions in our instrument, the acetonitrile pressure can be maintained within $\pm 5 \times 10^{-6}$ Pa, but for the purpose of observing its effect on the I–M reaction spectra, the acetonitrile pressure was varied from 2.0×10^{-5} Pa to 3.9×10^{-5} Pa. Tables 4 and 5 show the parent ion and

Table 5
Percentage of total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$ and $(ML + 2CH_3CN)^{2+}$) ions for the 2010 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with varying pressures of acetonitrile (temperature: 301 ± 1 K; He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$	$(ML + 2CH_3CN)^{2+}$
$(2.0 \pm 0.4) \times 10^{-5}$ Pa			
$Ni(DIEN\text{-}(imi)_2)^{2+}$	4 ± 2	95 ± 1	0.7 ± 0.8
$Ni(DIEN\text{-}(THF)_2)^{2+}$	0.5 ± 0.3	93 ± 2	7 ± 2
$Cu(DIEN\text{-}(imi)_2)^{2+}$	86 ± 3	14 ± 3	–
$Cu(DIEN\text{-}(THF)_2)^{2+}$	36 ± 4	60 ± 3	3.1 ± 0.7
$(2.8 \pm 0.4) \times 10^{-5}$ Pa			
$Ni(DIEN\text{-}(imi)_2)^{2+}$	3 ± 3	93 ± 2	7.7 ± 0.3
$Ni(DIEN\text{-}(THF)_2)^{2+}$	0.1 ± 0.1	86 ± 4	14 ± 4
$Cu(DIEN\text{-}(imi)_2)^{2+}$	83 ± 8	17 ± 8	–
$Cu(DIEN\text{-}(THF)_2)^{2+}$	26 ± 2	70 ± 2	4.2 ± 0.2
$(3.9 \pm 0.4) \times 10^{-5}$ Pa			
$Ni(DIEN\text{-}(imi)_2)^{2+}$	0.9 ± 0.1	95.7 ± 0.4	3.4 ± 0.4
$Ni(DIEN\text{-}(THF)_2)^{2+}$	0.4 ± 0.2	85 ± 3	14 ± 4
$Cu(DIEN\text{-}(imi)_2)^{2+}$	76 ± 8	24 ± 8	–
$Cu(DIEN\text{-}(THF)_2)^{2+}$	21 ± 8	72 ± 5	7 ± 2

Table 6
Equilibrium constants for the reactions of the Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at different pressures (temperature: 301 ± 1 K; He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa)

Acetonitrile pressure (Torr)	DIEN-$(imi)_2$		DIEN-$(THF)_2$	
	Ni(II)	Cu(II)	Ni(II)	Cu(II)
$(2.0 \pm 0.4) \times 10^{-5}$ Pa	90 ± 40	0.17 ± 0.03	>300[a]	2.2 ±0.5
$(2.8 \pm 0.4) \times 10^{-5}$ Pa	190 ± 40	0.2 ± 0.1	>300[a]	2.9 ± 0.5
$(3.9 \pm 0.4) \times 10^{-5}$ Pa	>300[a]	0.4 ± 0.1	>300[a]	3.6 ± 0.9

[a] The fitting of the data for these complexes failed to provide a non-negative value for k_{diss}, so the equilibrium constant was estimated from mass spectra taken under conditions in which the equilibrium was established.

product ion intensities for the reactions of acetonitrile with the Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$. The general trend in both tables is that as the acetonitrile pressure is raised the intensities of the product ions relative to the parent ion intensities increase. In Table 4 this is most clearly seen by following the relative intensities of the product and parent ions from the reaction of Ni(DIEN-$(THF)_2)^{2+}$ with acetonitrile for 110 ms. The intensity of the parent ion (ML^{2+}) changes from 78 to 52% over the pressure range of 2.0×10^{-5} Pa and 3.9×10^{-5} Pa, while the product ion intensity (($ML + CH_3CN)^{2+}$) changes from 22 to 48%. As expected, upon increasing the acetonitrile pressure, the reaction rate increases so that more product ions are formed and more parent ions are reacted away during the 110 ms reaction period.

Increasing the acetonitrile pressure should increase the resulting equilibrium constant also as the equilibrium is shifted toward product with the addition of more reactant. Observing the product ion intensities after a 2010 ms reaction time demonstrates this most clearly. In Table 5, for example, the parent ion intensities of Cu(DIEN-$(imi)_2)^{2+}$ vary from 85 to 76%, while the product ion intensities range from 15 to 24% over the acetonitrile pressure range studied. Table 6 shows the equilibrium constants calculated for each of the complexes shown in Table 5. As expected, the equilibrium constants increase as the pressure of acetonitrile increases.

3.2. Effect of helium pressure on product ion intensities

The helium pressure should also affect the spectra observed after reacting the different metal complexes with acetonitrile. As mentioned before these reactions are three-body association reactions that rely on the collisional cooling of helium to stabilize the product ion. The reaction rates should then be affected by the amount of helium in the vacuum system. Tables 7 and 8 show the effect of different helium pressures on the parent and product ion intensities for a 110 and 2010 ms reaction period, respectively. From Table 7, it is clear that increasing the helium pressure has a noticeable affect on the observed ion intensities after 110 ms. For example, the parent ion intensities for the Ni(DIEN-$(imi)_2)^{2+}$ complex decrease from 95 to 76%, while the product ion intensities increase from 5 to 24% over a helium pressure range of 4.7×10^{-3} Pa and 1.29×10^{-2} Pa. This trend and the reaction rates shown in Table 7 indicate that the addition of helium facilitates collisional cooling of the complex/acetonitrile adduct, allowing product ions to be formed more rapidly.

In contrast to the data in Table 7, a close examination of Table 8 demonstrates that increasing the helium pressure results in no clear trend in the parent and product ion intensities after a 2010 ms reaction time. The reaction of acetonitrile with Cu(DIEN-$(imi)_2)^{2+}$ seems to have a vague trend of decreasing product ion intensity as the helium pressure increases, but the relatively large standard deviations associated with these measurements add ambiguity to any possible trend. The equilibrium constants of these reactions as a function of helium pressure (Table 9) more clearly demonstrate the absence of a clear trend. The lack of a relationship between the helium pressure and the parent and product ion intensities following a 2010 ms reaction with acetonitrile is not unexpected given the suspected reaction dynamics (vide infra).

Table 7
Reaction rate constants and percentage of the total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$) ions for the 110 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at various helium pressures (temperature: 301 ± 1 K; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$	Rate constant (10^{-10} cm^3 per molecule s^{-1})[a]
$(4.7 \pm 0.6) \times 10^{-3}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	95.0 ± 0.4	5.0 ± 0.4	1.8 ± 0.5
Ni(DIEN-$(THF)_2)^{2+}$	72 ± 17	28 ± 17	6.0 ± 1.8
Cu(DIEN-$(imi)_2)^{2+}$	99 ± 1	1 ± 1	0.5 ± 0.2
Cu(DIEN-$(THF)_2)^{2+}$	94.2 ± 0.2	5.8 ± 0.2	1.5 ± 0.1
$(8.3 \pm 0.8) \times 10^{-3}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	92 ± 1	8 ± 1	2.5 ± 0.7
Ni(DIEN-$(THF)_2)^{2+}$	40 ± 7	60 ± 7	7.7 ± 0.3
Cu(DIEN-$(imi)_2)^{2+}$	98.2 ± 0.8	1.8 ± 0.8	0.4 ± 0.2
Cu(DIEN-$(THF)_2)^{2+}$	95.1 ± 0.2	4.9 ± 0.2	1.2 ± 0.1
$(1.29 \pm 0.02) \times 10^{-2}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	76 ± 1	24 ± 1	4.4 ± 0.4
Ni(DIEN-$(THF)_2)^{2+}$	52 ± 13	48 ± 13	9.5 ± 0.1
Cu(DIEN-$(imi)_2)^{2+}$	97 ± 1	3 ± 1	0.7 ± 0.3
Cu(DIEN-$(THF)_2)^{2+}$	85 ± 2	15 ± 2	3.1 ± 0.7

[a] These values were obtained by fitting Eq. (1) to the experimental data.

Table 8
Percentage of the total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$ and $(ML + 2CH_3CN)^{2+}$) ions for the 2010 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at various helium pressures (temperature: 301 ± 1 K; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$	$(ML + 2CH_3CN)^{2+}$
$(4.7 \pm 0.6) \times 10^{-3}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	4 ± 2	94 ± 1	2 ± 1
Ni(DIEN-$(THF)_2)^{2+}$	1 ± 1	83 ± 6	16 ± 6
Cu(DIEN-$(imi)_2)^{2+}$	74 ± 11	26 ± 11	–
Cu(DIEN-$(THF)_2)^{2+}$	19.7 ± 0.9	74 ± 1	6.3 ± 0.4
$(8.3 \pm 0.8) \times 10^{-3}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	6 ± 5	91 ± 6	2.9 ± 0.8
Ni(DIEN-$(THF)_2)^{2+}$	0.2 ± 0.1	82 ± 10	17 ± 10
Cu(DIEN-$(imi)_2)^{2+}$	79 ± 9	21 ± 9	–
Cu(DIEN-$(THF)_2)^{2+}$	32.3 ± 0.3	63.7 ± 0.5	3.9 ± 0.6
$(1.29 \pm 0.02) \times 10^{-2}$ Pa			
Ni(DIEN-$(imi)_2)^{2+}$	0.9 ± 0.1	95.7 ± 0.4	3.4 ± 0.4
Ni(DIEN-$(THF)_2)^{2+}$	0.4 ± 0.2	85 ± 3	14 ± 4
Cu(DIEN-$(imi)_2)^{2+}$	85 ± 2	15 ± 2	–
Cu(DIEN-$(THF)_2)^{2+}$	21 ± 7	72 ± 5	7 ± 2

3.3. Effect of temperature on product ion intensities

The kinetics of chemical reactions and the equilibrium ratio of products and reactants are affected by temperature. Consequently, we varied the temperature of the vacuum system on the mass spectrometer and observed the effect on the reaction dynamics. Tables 10 and 11 demonstrate how the change in temperature affects the parent and product ion intensities after 110 and 2010 ms reaction periods, respectively. The general tendency is that as the temperature

Table 9
Equilibrium constants for the reactions of the Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at different helium pressures (temperature: 301 ± 1 K; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Helium pressure (Torr)	DIEN-$(imi)_2$		DIEN-$(THF)_2$	
	Ni(II)	Cu(II)	Ni(II)	Cu(II)
$(4.7 \pm 0.6) \times 10^{-3}$ Pa	100 ± 30	0.4 ± 0.2	>300[a]	2.6 ± 0.4
$(8.3 \pm 0.8) \times 10^{-3}$ Pa	129 ± 3	0.29 ± 0.1	>300[a]	2.3 ± 0.1
$(1.29 \pm 0.02) \times 10^{-2}$ Pa	116 ± 22	0.39 ± 0.1	>300[a]	4 ± 1

[a] The fitting of the data for these complexes failed to provide a non-negative value for k_{diss}, so the equilibrium constant was estimated from mass spectra taken under conditions in which the equilibrium was established.

Table 10
Reaction rate constants and percentage of the total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$) ions for the 110 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at various temperatures (He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$	Rate constant (10^{-10} cm^3 per molecule s^{-1})[a]
301 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	76 ± 1	24 ± 1	4.4 ± 0.4
Ni(DIEN-$(THF)_2)^{2+}$	52 ± 13	48 ± 13	9.5 ± 0.4
Cu(DIEN-$(imi)_2)^{2+}$	97 ± 1	3 ± 1	0.7 ± 0.1
Cu(DIEN-$(THF)_2)^{2+}$	85 ± 2	15 ± 2	3.1 ± 0.7
303 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	89 ± 1	11 ± 1	3.2 ± 0.3
Ni(DIEN-$(THF)_2)^{2+}$	53 ± 10	47 ± 10	7.4 ± 0.4
Cu(DIEN-$(imi)_2)^{2+}$	97.1 ± 0.7	2.9 ± 0.7	0.6 ± 0.1
Cu(DIEN-$(THF)_2)^{2+}$	89 ± 4	11 ± 4	2.3 ± 0.2
305 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	89 ± 2	11 ± 2	2.9 ± 0.2
Ni(DIEN-$(THF)_2)^{2+}$	73 ± 11	27 ± 11	4 ± 2
Cu(DIEN-$(imi)_2)^{2+}$	97 ± 1	3 ± 1	0.4 ± 0.1
Cu(DIEN-$(THF)_2)^{2+}$	89 ± 2	11 ± 2	2.5 ± 0.4

[a] These values were obtained by fitting Eq. (1) to the experimental data.

increases the parent ion intensities increase and the product ion intensities decrease. This trend means that the reaction rates slow down (see Table 10) with increasing temperature, and the equilibrium constants decrease as well (Table 12). This result is not surprising because in order for a product ion to form it needs to be stabilized by collisions with helium, and at higher temperatures this stabilization is hindered.

4. Discussion

A comparison of Tables 2 and 3 suggests that allowing the reaction to reach an equilibrium (i.e. reaction time of 2010 ms) results in better reproducibility than allowing the reaction to go for only 110 ms. In fact, within the experimental error the parent and product ion intensities of all the complexes except those of DIEN-$(THF)_2$ and DIEN-(THF)(thioether) were distinct after a 2010 ms reaction with acetonitrile. The lower precision of the results obtained after a 110 ms reaction can be understood by considering the kinetics of these reactions. After 110 ms, the reaction of a given metal complex with acetonitrile is far from equilibrium, so the parent ion intensity is rapidly changing with time. In fact, taking the derivative of plots like Fig. 2 indicates that the slopes of these curves are greatest at 110 ms. This means that at this point in the reaction the parent and product ion intensities are most sensitive to any fluctuations in the experimental

Table 11
Percentage of the total ion intensity of the parent (ML^{2+}) and product ($(ML + CH_3CN)^{2+}$ and $(ML + 2CH_3CN)^{2+}$) ions for the 2010 ms reactions of Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at various temperatures (He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Complex	ML^{2+}	$(ML + CH_3CN)^{2+}$	$(ML + 2CH_3CN)^{2+}$
301 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	0.9 ± 0.1	95.7 ± 0.4	3.4 ± 0.4
Ni(DIEN-$(THF)_2)^{2+}$	0.4 ± 0.2	85 ± 3	14 ± 4
Cu(DIEN-$(imi)_2)^{2+}$	76 ± 8	24 ± 8	
Cu(DIEN-$(THF)_2)^{2+}$	21 ± 7	72 ± 5	7 ± 2
303 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	2.2 ± 0.5	95.6 ± 0.3	2.1 ± 0.2
Ni(DIEN-$(THF)_2)^{2+}$	0.3 ± 0.1	86 ± 2	14 ± 2
Cu(DIEN-$(imi)_2)^{2+}$	77 ± 3	23 ± 3	
Cu(DIEN-$(THF)_2)^{2+}$	25 ± 3	72 ± 2	4 ± 1
305 ± 1 K			
Ni(DIEN-$(imi)_2)^{2+}$	1.7 ± 0.1	96.2 ± 0.1	2.0 ± 0.2
Ni(DIEN-$(THF)_2)^{2+}$	2 ± 2	92 ± 3	6 ± 6
Cu(DIEN-$(imi)_2)^{2+}$	83 ± 5	17 ± 5	
Cu(DIEN-$(THF)_2)^{2+}$	30 ± 4	66 ± 3	3.8 ± 0.7

Table 12
Equilibrium constants for the reactions of the Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ with acetonitrile at different temperatures (He pressure: $(1.29 \pm 0.02) \times 10^{-2}$ Pa; acetonitrile pressure: $(3.9 \pm 0.4) \times 10^{-5}$ Pa)

Temperature (K)	DIEN-$(imi)_2$		DIEN-$(THF)_2$	
	Ni(II)	Cu(II)	Ni(II)	Cu(II)
301 ± 1	>300[a]	0.4 ± 0.1	>300[a]	3.6 ± 0.9
303 ± 1	190 ± 90	0.4 ± 0.1	>300[a]	3.3 ± 0.6
305 ± 1	60 ± 30	0.3 ± 0.1	>300[a]	2.5 ± 0.3

[a] The fitting of the data for these complexes failed to provide a non-negative value for k_{diss}, so the equilibrium constant was estimated from mass spectra taken under conditions in which the equilibrium was established.

conditions. The greater relative standard deviations in the data taken at 110 ms reflect this greater sensitivity.

The reactions of acetonitrile with the Ni(II) and Cu(II) complexes of DIEN-$(imi)_2$ and DIEN-$(THF)_2$ were studied while varying different experimental parameters in order to better understand the degree to which these factors affect the reaction dynamics. Studying the effects of reagent gas (i.e. acetonitrile) pressure, helium pressure, and temperature should provide insight into which of these experimental variables are most important to control in order to maximize precision. Based on the data in Tables 4–12, all three factors have a noticeable affect on the parent and product ion intensities after a 110 ms reaction, while only the acetonitrile pressure and the temperature have a clear effect on the parent and product ion intensities after a 2010 ms reaction. To better understand why this is the case, it is helpful to use the reaction rates to explain the results obtained after a 110 ms reaction time and to use the equilibrium constants to explain the results for the 2010 ms reaction time.

4.1. Reactions for 110 ms

Because after 110 ms the reaction of the metal complexes with acetonitrile is far from an equilibrium, the forward reaction rate has a big impact on the observed parent and product ion intensities. Eqs. (2)–(4) show the reaction of the metal complex is first order with respect to the reagent gas. Such a case means that the reagent gas will have a direct impact on the observed reaction rates. Indeed, this is seen experimentally as

the parent and product ion intensities change significantly (Table 4) when the acetonitrile pressure is about doubled from 2.0×10^{-5} Pa and 3.9×10^{-5} Pa. The effect is most apparent on the most reactive of the complexes, Ni(DIEN-$(THF)_2)^{2+}$. The parent ion intensity in this case varies from 78 to 52% and the product ion intensity varies from 22 to 48% as the acetonitrile pressure is doubled. In contrast, the impact of doubling the acetonitrile pressure is less for the least reactive complex, Cu(DIEN-$(imi)_2)^{2+}$. The parent ion intensity for this complex only changes from 99 to 97%, and the product ion intensity only changes from 1 to 3%. The very distinct rate constants for Ni(DIEN-$(THF)_2)^{2+}$ and Cu(DIEN-$(imi)_2)^{2+}$ explains these differences.

The reaction rate is also first order with respect to the helium pressure, and the parent and product ion intensities after a 110 ms reaction vary in a manner similar to the experiments where acetonitrile is increased. Again, the biggest variation is seen with the most reactive complex, Ni(DIEN-$(THF)_2)^{2+}$, and the least variation is seen with Cu(DIEN-$(imi)_2)^{2+}$ (see Table 7). In these three-body reactions, the initial encounter between acetonitrile and the metal complex results in an intermediate that contains too much energy to be stable. Helium acts to collisionally remove energy from this excited intermediate so that a stable product ion can eventually form. As the helium pressure is increased the reaction rates should also increase, and indeed the rate constants in Table 7 clearly demonstrate this. The increasing magnitudes of the reaction rate constants as a function of increasing helium pressure provide confirmation that our assumption about the three-body nature of these I–M reactions is valid.

Changing the helium pressure could also have an impact on the kinetic energies and temperatures of the parent ions. The sensitivity of I–M reaction rates to ion kinetic energy [39] and temperature [40] is well known. The average kinetic energy of the ions in this study is likely a few eV or less [41–43] because of the damping of ion motion by collisions with helium. The slight changes to the helium pressure in this study are unlikely to affect ion motion enough to significantly change ion kinetic energies. The effect of helium pressure on the temperature of ions in a quadrupole ion trap has not been well studied, but several investigators have provided good evidence that ions achieve thermal temperatures while trapped in the presence of helium [44–47]. The small helium pressure changes in this work result in only about a 50% change in the number of ion collisions with helium per unit time. This relatively small change in the number of collisions is unlikely to significantly affect the temperature of the ions.

The temperature of the vacuum system also has an impact on the parent ion and product ion intensities measured after a 110 ms reaction period. Increasing the temperature of the vacuum system will increase the temperature of the helium atoms, making them less effective at collisionally cooling the excited intermediate ion. The result should be lower parent and product ion intensities and lower reaction rate constants as Table 10 demonstrates. Again, the most susceptible to the temperature changes is Ni(DIEN-$(THF)_2)^{2+}$, and the least susceptible is Cu(DIEN-$(imi)_2)^{2+}$.

4.2. Reactions for 2010 ms

For all metal complexes studied so far, a 2010 ms reaction time with acetonitrile is adequate for an equilibrium to be established. As a result, the equilibrium constant and the factors that affect it are best for explaining the results obtained at this reaction time. Clearly the acetonitrile pressure will have an impact on the equilibrium constant as it effects the magnitude of the forward reaction rate constant (k_f) and has no effect on the reverse reaction rate constant (k_{diss}). Because the equilibrium constant can be evaluated by taking the ratio of these rate constants (i.e. $K_{eq} = k_f/k_{diss}$), an increase in the acetonitrile pressure results in an increase in the equilibrium ratio of the product to parent ions. Table 5 shows the impact of increasing the acetonitrile pressure on the parent and product ion intensities, and Table 6 more clearly shows the change in the magnitude of the equilibrium constant.

In contrast, increasing the helium pressure has little effect on the equilibrium ratios of the parent and product ions. By applying the steady-state approximation k_f and k_{diss} can be evaluated as a function of the rate constants in Eqs. (3) and (4). The equations that result are (Eqs. (5)–(7)):

$$k_f = \frac{k_a k_s [R][M]}{k_b + k_s[M]} \tag{5}$$

$$k_{diss} = \frac{k_b k_{ac}[M]}{k_b + k_s[M]} \tag{6}$$

$$K_{eq} = \frac{k_a k_s [R]}{k_b k_{ac}} \quad (7)$$

Upon determining the equilibrium constant (Eq. (7)) by dividing k_f by k_{diss}, the expression for K_{eq} becomes independent of the helium pressure (M). It is not surprising then that the data in Tables 8 and 9 are independent of the helium pressure. Thus, slight fluctuations in the helium pressure should have little effect on the reproducibility of the parent and product ion intensities as long as these values are determined after an equilibrium has been established.

The temperature, on the other hand, should have an effect on the parent and product ion intensities at equilibrium. The effect of temperature on the equilibrium constants is well established. In fact, van't Hoff plots, where the natural log of the equilibrium constant is plotted against the reciprocal temperature, are a common means of evaluating the enthalpy and entropy of a reaction that reaches an equilibrium. The addition of acetonitrile to the coordinatively unsaturated complexes in this study is an exothermic reaction with a negative enthalpy. Consequently, increasing the temperature should decrease the equilibrium constant and thus decrease the extent of the reaction. Indeed, Table 11 shows that the product ion intensities do decrease as the temperature is increased. Most clearly the intensities of the product ions that show the addition of a second acetonitrile are decreased while the parent ion intensities increase. Because the slopes of van't Hoff plots are directly related to the enthalpy of the reaction, the metal complexes that bind acetonitrile most strongly (and thus have the largest enthalpy terms) should be affected most by the change in temperature. The reaction of $Ni(DIEN\text{-}(imi)_2)^{2+}$ with acetonitrile demonstrates this fact as its equilibrium constant changes most drastically. In contrast, $Cu(DIEN\text{-}(imi)_2)^{2+}$, which binds acetonitrile weakly, has the least change in the equilibrium constant as the temperature is increased. Unfortunately, due to the difficulty in accurately knowing the temperature inside the vacuum system, more quantitative enthalpy and entropy values are not possible with the current data.

As evident from the data in Tables 2 and 3, parent and product ion intensities are more reproducible when evaluated after a 2010 ms reaction period than when evaluated at a shorter reaction time. For all the reactions studied to date, an equilibrium is established by this time. Therefore, careful attention needs to be paid to the factors most likely to affect the equilibrium constant and thus the parent and product ion intensities. The reagent gas pressure and the temperature are the dominant experimental variables that hinder the precision of any measurement based on these ion intensities. Careful control of the reagent gas pressure is most critical because its level is directly related to the resulting equilibrium constant while the temperature is related via a logarithmic term. Future steps will be taken to increase the reproducibility of the reagent gas pressure in the vacuum system.

5. Conclusions

I–M reactions of metal complex ions with a reagent gas such as acetonitrile seems to be a promising means of using quadrupole ion trap mass spectrometry to obtain information about the functional groups bound to a metal. The simple adduction of the reagent gas to the metal complex ion provides a product ion with a significantly different m/z ratio, whose intensity is dependent upon the coordination environment around the metal. The experiments performed in this work clearly show that measuring the relative parent and product ion intensities after a reaction time long enough to establish an equilibrium could provide a reproducible means of elucidating the number and types of functional groups bound to a metal. This approach provides two main advantages over the typical means of gathering structural information by MS (i.e. using CID). First, CID data might indicate that a particular functional group is present, but it cannot necessarily confirm that the functional group binds the metal in the complex. And second, CID involves heating an ion via collisions that could result in the scrambling of the metal coordination sphere, while I–M reactions provide a much more gentle analysis.

In this study the reagent gas pressure and the temperature of the vacuum system were shown to have the biggest effects on the dynamics of these reactions, while the helium buffer gas pressure had little effect. The reagent gas pressure seems to have the biggest impact on the reactions, and thus careful control of

its level is needed to ensure the greatest degree of precision. Finally, the metal complexes with the highest reactivity were shown to have inherently the lowest precision because they are the most sensitive to slight changes in reagent gas pressure and temperature. Future work will assess ways to better control the reagent gas pressure and determine if other reagent gases are more analytically useful. Also, efforts to establish a I–M reaction database for metal complex ions are underway in order to determine if this procedure has more general applicability for coordination structure determination.

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