Gas-Phase Solvation Behavior of Ni(II) in Water/*N*,*N*-Dimethylformamide Mixtures

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Electrospray ionization−mass spectrometry (ESI-MS) is used to investigate the complexation of nickel(II) by *N*,*N*-dimethylformamide (DMF) in different water/DMF mixtures. The types of solvated cations observed are independent of the solvent composition and are part of the series $[Ni(DMF)_n]^{2+}$ with $n = 2-6$ and $[Ni(DMF)_nX]^+$ with $n = 1-4$ (where X = Cl, Br, NO_3). The number of ligands, n, and thus the extent of solvation depends on the cone voltage (U_C) of the ESI source. At low U_C multiply ligated ions prevail, whereas ligation drops with rising U_C and further increase of U_C causes dissociation of the solvent molecules as well as reduction of Ni(II) to Ni(I). The collision-induced dissociation (CID) spectra of the multiply ligated ions $[Ni(DMF)_n]^{2+}$ with $n \geq 3$ and $[Ni(DMF)_nX]^+$ with $n \geq 2$ show only losses of neutral DMF ligands. Quite different is the behavior of the bisligated ions $[Ni(DMF)_2]^{2+}$ and $[Ni(DMF)X]^+$. In the CID spectrum of $[Ni(DMF)_2]^{2+}$, electron transfer from DMF to the metal leads to the reduced complex $[Ni(DMF)]^+$ concomitant with ionized DMF^+. Charge-stripping spectra of mass-selected monocations $[Ni(DMF)_n]^+$ ($n = 1, 2$) confirm that the dication $[Ni(DMF)_2]^{2+}$ is stable, whereas monoligated $[Ni(DMF)]^{2+}$ appears to be intrinsically unstable toward Coulomb explosion. In the CID spectra of $[Ni(DMF)Cl]^+$ and $[Ni(DMF)Br]^+$, bond activation of the solvent takes place, and in the case of $[Ni(DMF)NO_3]^+$ the formation of a cationic species is observed which formally corresponds to the solvated metal-oxide cation $[(DMF)NiO]^+$.

Introduction

Electrospray ionization (ESI) is a soft ionization technique, developed by Fenn and co-workers,[1] which allows the transfer of solvated ions from solution to the gas phase. Quite often, ESI leads to multiply charged ions, thereby reducing the mass-to-charge ratio of the analyte. Therefore, the ESI−mass spectrometry (MS) is particularly useful for the study of large and/or labile molecules such as proteins, enzymes, and polymers.[2−9] In addition, ESI-MS has widely been used for the detection and analysis of doubly and triply charged transition-metal complexes and it can provide information concerning the structure, stoichiometry, and the metal's oxidation state for the multiply charged ions which are difficult to probe by other techniques.

In the initial stage of the ESI process, large charged droplets are formed at atmospheric pressure by nebulization. Evaporation of the solvent leads to shrinkage of the droplets, thereby increasing the charge density until solvated ions are formed by charge separation ("Coulomb explosion"). The solvated ions move across an electric field and pass to the mass spectrometer through a skimmer forming a molecular beam which contains various ions in aggregation with solvent molecules. Solvent evaporation can be further aided by an additional "drying" gas (usually nitrogen) in the interface region of the instrument. It is known that the product ions observed in the gas phase are related to the chemical nature of the analyzed solution (composition, pH of the solvent), the source temperature, the composition of the drying gas, and the capillary voltage. Spence et al.[10] proposed a new method for controlled formation of transition-metal complexes which separates the electrospray ionization process from the complex formation. In this method, the ions are first completely desolvated by collisions and then, in a time-delayed process, reformed by introducing a selective solvent vapor, seeded in nitrogen, in the expansion region. This method is useful for the formation of complexes with compounds which are unsuitable as electrospray solvents.

Complexes of multiply charged metal ions ML_m^{n+} are of interest due to the rich chemistry involved, e.g., electron and proton transfers, ligand-exchange reactions, or even bond activation of the solvent molecules.[11,12] Two extreme types of ML_m^{n+} complexes can be distinguished−those formed by polar and/or very polarizable ligands, e.g., water and *N*,*N*-dimethylformamide (DMF), and those formed by weakly coordinating ligands with high ionization energies, e.g., rare gases. The complexes of the first type are stabilized by strong ion/dipole and ion/induced-dipole interactions, thereby leading to discrete energy minima for the ML_m^{n+} species even if charge separation to yield $ML_{m-1}^{(n-1)+} + L^+$ is exothermic. Although the bond energies are relatively small, the complexes of the second type are stable because the charge-separation asymptotes themselves are endothermic due to the often small differences between the ionization energies of the ligands and the metal ions.[13,14] As far as ML_m^{2+} dications are concerned, the second ionization energies of most metals exceed the first ionization energies of typical solvent molecules (8−13 eV) such that electron transfer from the neutral ligand to the metal ion is exothermic. In this case the complexes are metastable and they owe their existence to an avoided crossing of the repulsive charge-separation asymptote and the attractive interactions of M^{2+} with L.[11] In addition, the size of the coordinating molecule may play a role in multiply ligated metal-ion complexes. Large steric demand of the ligand is usually associated with decreasing coordination numbers of the metal ion.[15]

Many researchers have used ESI-MS for the investigation of multiply charged metal ions complexed by organic molecules in the gas phase. For example, Katta et al.[16] studied Ru(II)

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complexed by 2,2-bipyridyl and 1,10-phenanthroline, Blades et al.[17] investigated tricationic metal complexes of DMSO and DMF, Ross et al.[18] studied bivalent transition-metal cations complexed by 8-hydroxyquinoline, *N*,*N*-diethyldithiocarbamate, diphenylthiocarbazone, and dimethylglyoxime, Kohler and Leary[19] investigated Co(II), Mn(II), Ca(II), and Sr(II) complexed by oligosaccharides as well as acetonitrile, Shvartsburg[20,21] studied trivalent metal cations complexed by DMSO and 4-hydroxy-4-methyl-2-pentanone, and Shvartsburg and Siu[22] studied metal dication complexes with water. Complexation of Zn(II) with glycine has been investigated by Rogalewicz et al.,[23−25] Eu(III) and Ln(III) with 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl) pyridines by Colette et al.,[26,27] Co(II), Ni(II), Cu(II), Zn(II), Mn(II), Fe(II) with flavonoids by Satterfield and Brodbelt,[28] Cu(II) with glycine and glycylglycine by Seto and Stone,[29] and Fe(III) with di-hydroxamic acids by Spasojevic et al.[30] The ESI-MS technique was also used by Andersen and co-workers[31] for the characterization of the oxo-bridged dinuclear complexes of Fe(III), Mn(IV), and V(IV).

The investigation of Ni(II) complexed by water using ESI-MS has been the subject of several studies,[32,33] but nickel complexes of DMF have not been examined so far. Previous experience with the condensed-phase properties of nickel(II) salts in water/DMF[34] and water/methanol mixtures[35] led us to an investigation of solutions of $NiCl_2$, $NiBr_2$, $Ni(NO_3)_2$, and $NiSO_4$ in mixtures of water and DMF using ESI-MS; methanol is used as a cosolvent improving the spray conditions.[36] Moreover, reactions involving the DMF molecule (which has one of the simplest peptide bonds) can be used as a model to understand the behavior of more complicated biomolecules complexed to multiply charged metal ions.[37,38]

DMF is a widely used as an aprotic polar solvent with a large dipole moment ($\mu = 3.8$ D),[39] a strong electron-pair donating capacity (DN = 26.6 kcal·mol^{-1}),[39] and a high dielectric constant ($\epsilon = 38.5/20$ °C).[34] It has a peptide group with the two basic centers, the oxygen of carbonyl and the nitrogen. In the liquid state, DMF shows self-association due to dipole/dipole interactions creating open and cyclic dimers as well as higher oligomers.[40−42] In aqueous mixtures, DMF gives rise to two- or three-dimensional networks through hydrogen bonds with the consequence that the mixtures display negative deviations from ideality.[34] NMR studies[43] have shown that the oxygen of the carbonyl group and not the nitrogen atom forms hydrogen bonds with the water molecules and that these bonds are stronger than the hydrogen bonds between water molecules.[44,45]

As far as transition-metal complexes are concerned, DMF behaves as a monodentate ligand which readily forms symmetrical six-coordinate octahedral complexes with nickel(II) via the oxygen of the carbonyl group.[46] Matwiyoff[47] proposed that two modes of coordination of DMF around a metal cation are possible, a linear and the angular one. Studies in the condensed-phase indicate that no significant steric effects are operative when DMF approaches the nickel(II) ion,[48] and the Ni−O bond lengths in Ni(II)−DMF complexes were found to be similar to those in Ni(II)−water complexes.[49]

Experimental Section

All ESI experiments were performed with a VG BIO-Q instrument which consists of an ESI source followed by a mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole).[50] In all experiments, the instrument parameters were optimized for maximum ion abundances. Typical values were the following: capillary voltage 3.6 kV, HV lens (counter electrode) 30 V, cone voltage 10−80 V, RF lens 0.1 V, skimmer 1.0 V, and skimmer-lens offset 5 V. In the experiments, millimolar solutions of nickel(II) salts were introduced via a syringe pump (flow rate 5 μL/min) to the stainless steel capillary of the ESI source. Nitrogen was used as nebulizing and drying gas at a source temperature of 90 °C. The mass spectra of the ions formed were obtained at unit mass resolution by scanning Q1.

Collision-induced dissociation (CID) experiments were performed with xenon at various collision energies ($E_{\mathrm{Lab}} = 0-25$ eV) and a pressure of ca. 4×10^{-4} mbar, which is considered to correspond to single-collision conditions. The collision energies were converted to the center-of-mass frame, $E_{\mathrm{CM}} = m/(M + m)E_{\mathrm{Lab}}$, where m and M are the masses of the collision gas and the ionic species, respectively. For CID, the ions of interest were mass-selected using Q1, interacted with xenon in the hexapole collision cell, while scanning Q2 to monitor the ionic fragments. As pointed out previously, the VG-BioQ does not allow us to directly extract quantitative threshold information from CID experiments due to several limitations of the commercial instrument.[50] Even at $E_{\mathrm{Lab}} = 0$ V, for example, nonnegligible ion decay is observed which is attributed to collision gas being present not only in the hexapole but also in the focusing regions between the mass analyzers. On an empirical basis, the energy dependence of the CID spectra can be approximated by simple sigmoid functions which we use for the determination of phenomenological appearance energies (AEs) of the fragment ions in the E_{CM} frame.[51] Note, however, that the AEs given below do not directly correspond to thermochemical thresholds of the respective ion dissociations.

Ligated nickel(II) ions were generated from $NiCl_2$, $NiBr_2$, $Ni(NO_3)_2$, and $NiSO_4$ dissolved in water/DMF mixtures (1.0% w/w DMF and 50.0% w/w DMF). The ions which contain nickel are readily identified by their characteristic isotope envelopes. Unless noted otherwise, we investigated the complexes of the most abundant ^{58}Ni isotope, thereby improving signal-to-noise ratios and avoiding possible isobaric interferences by other isotope compositions.

In addition, charge-stripping (CS) spectra of $[Ni(DMF)_n]^+$ monocations ($n = 1, 2$) were recorded with a modified VG-ZAB/HF/AMD-604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described elsewhere.[52] The ions of interest were generated by chemical ionization of DMF with either bis[cyclopentadienylnickel(I) carbonyl] or nickel(II) bis(hexafluoroacetylacetonate) as metal ion precursors. After acceleration to a kinetic energy of 8 keV, CS spectra were recorded by monitoring the ionic products formed upon collision of the mass-selected $Ni(DMF)_n^+$ monocations with oxygen.

N,*N*-Dimethylformamide (Merck, 99.9%) was spectral grade and the water was doubly distilled. Nickel chloride hexahydrate (Fluka, p.a. ≥ 98.0%), anhydrous nickel bromide (Aldrich, p.a. ≥ 98.0%), nickel nitrate hexahydrate (Fluka, p.a. ≥ 98.5%), and nickel sulfate hexahydrate (Fluka, p.a. ≥ 99.0%) were used without further purification.

Results and Discussion

The solvated nickel cations formed upon ESI of nickel(II) salts dissolved in water/DMF belong to the series $[Ni(DMF)_n]^{2+}$ with $n = 2-6$ and $[Ni(DMF)_nX]^+$ with $n = 1-4$ (where X = Cl, Br, NO_3) for both solvent compositions; the hexacoordinate monocations $[Ni(DMF)_5X]^+$ were observed only in traces. In addition, ESI leads to protonated DMF-clusters of the type $(DMF)_nH^+$ ($n = 1-3$). The influence of the solvent composition

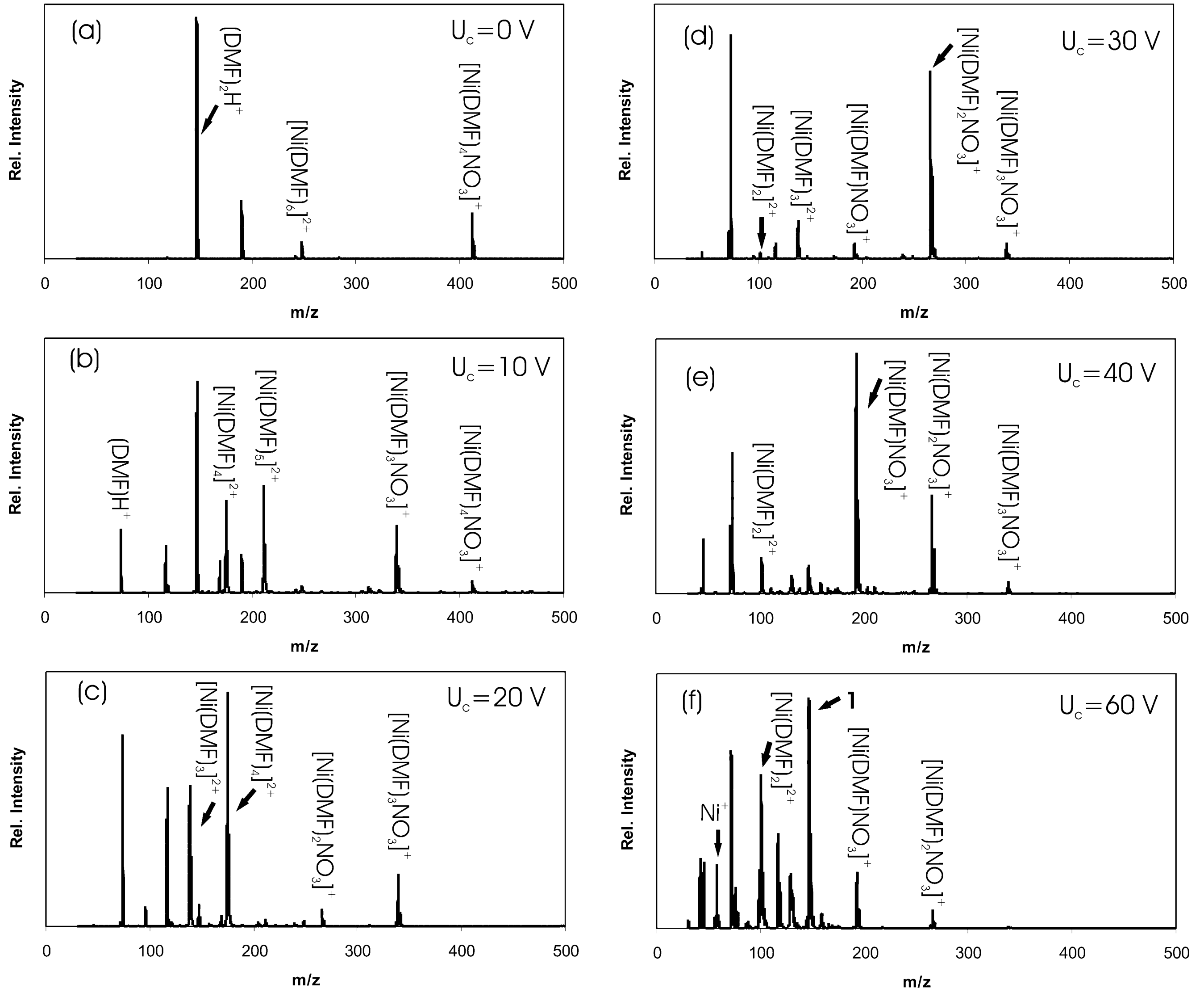

Figure 1. Electrospray mass spectra of $Ni(NO_3)_2$ in 1% w/w DMF at variable cone voltages (U_C).

on the fragmentation patterns of the mass-selected complexes was negligible. Pronounced effects of the counterion occur in the case of $NiSO_4$ as only complexes of the type $[Ni(DMF)_n]^{2+}$ were observed which is an obvious consequence of the divalent SO_4^{2-} counterion.

The absence of signals which correspond to hydrated nickel ions even at 1% w/w DMF demonstrates that the solvated nickel ions are far more stable with DMF than with water.[53-56] This finding is in agreement with condensed-phase data of Gritzner and Horzenberger[57] who observed that the enthalpy, the entropy, and the Gibbs free energy of transfer of the several dications from water to DMF are negative, indicating a preferential solvation of the ions by DMF.

The relative intensities of the solvated species were quite sensitive to the cone voltage (U_C) of the ESI source.[19] At low U_C, ionization is gentle and multiply ligated ions prevail, whereas smaller complexes are formed with rising U_C. Further increase of U_C causes dissociation of the solvent molecules as well as reduction to nickel(I). At low cone voltages, gas-phase ions are observed which also exist in the liquid phase (e.g., $[Ni(DMF)_6]^{2+}$ and $[Ni(DMF)_4Cl]^+$),[58] whereas enhanced cone voltages afford coordinatively unsaturated complexes formed via consecutive losses of solvent molecules (e.g., $[Ni(DMF)_2]^{2+}$ and $[Ni(DMF)Cl]^+$). As an example, the ESI mass spectra of $Ni(NO_3)_2$ in 1% w/w DMF at variable cone voltages are shown in Figure 1. At low cone voltages (0 and 10 V, Figures 1a and 1b), multiply ligated species prevail, i.e., the dications $[Ni(DMF)_6]^{2+}$, $[Ni(DMF)_5]^{2+}$, and $[Ni(DMF)_4]^{2+}$ as well as the monocations $[Ni(DMF)_4NO_3]^+$ and $[Ni(DMF)_3NO_3]^+$. Upon gradual rise of U_C (20 and 30 V, Figures 1c and 1d), the dication $[Ni(DMF)_3]^{2+}$ and the monocation $[Ni(DMF)_2NO_3]^+$ appear as new products. At about $U_C = 40$ V (Figure 1e), detachment of DMF ligands leads to the corresponding bisligated cations $[Ni(DMF)_2]^{2+}$ and $[Ni(DMF)NO_3]^+$. At elevated values of U_C (60 V, Figure 1f), dissociation of the bisligated cations takes place inter alia yielding the Ni(I) species $[Ni(DMF)]^+$ and finally bare Ni^+. Upon ESI of $Ni(NO_3)_2$ in water/DMF, an additional species **1** is observed in Figure 1f which is addressed in more detail further below.

Identical conclusions are derived from collision-induced dissociation (CID) of mass-selected $[Ni(DMF)_n]^{2+}$ and $[Ni(DMF)_nX]^+$ (with X = Cl, Br, NO_3). For $n \geq 3$ and $n \geq 2$, respectively, only sequential losses of neutral DMF ligands are observed which becomes more difficult as the number of ligands decreases. This is in agreement with observations of Dzidic and Kebarle[59] who demonstrated for hydrated metal ions that the bond energies are inversely related to the number of ligands. The two phenomena which decrease the ion/dipole interactions

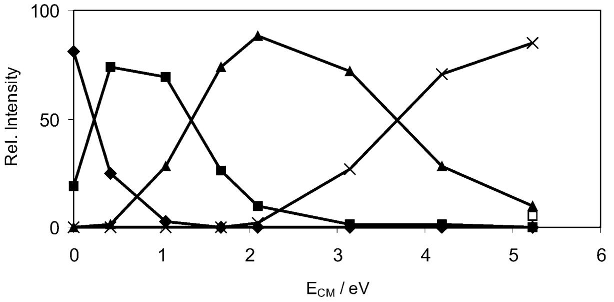

Figure 2. Relative ion intensities as a function of center-of-mass collision energies (E_{CM}) in the CID spectra of $[Ni(DMF)_6]^{2+}$. The symbols are denoted as follows: $[Ni(DMF)_6]^{2+}$ (♦), $[Ni(DMF)_5]^{2+}$ (■), $[Ni(DMF)_4]^{2+}$ (▲), $[Ni(DMF)_3]^{2+}$ (×), $[Ni(DMF)_2]^{2+}$ (□).

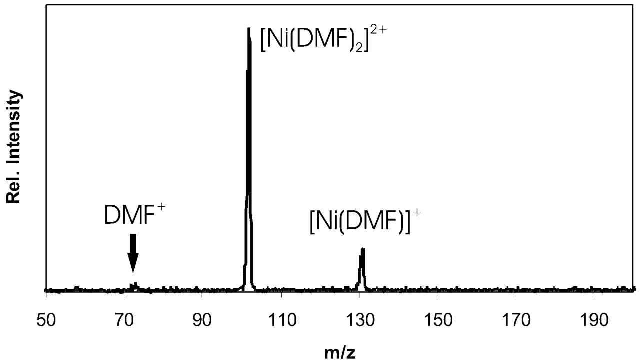

Figure 3. CID spectrum of mass-selected $[Ni(DMF)_2]^{2+}$ ($m/z = 102$) at $E_{CM} = 3.1$ eV.

TABLE 1: Selected Neutral Losses upon Collision of Mass-Selected $[Ni(DMF)_n]^+$ Monocations ($n = 1, 2$) Having 8 KeV Kinetic Energy with Oxygen as Target Gas[a]

	$-CH_3$	$-CH_2O$	$-DMF$	-2 DMF	M^{2+} [b]
$[Ni(DMF)]^+$	40	30	100	$-$[c]	$-$[d]
$[Ni(DMF)_2]^+$			100	3	40

[a] Intensities given relative to the base peak (100). [b] M^{2+} stands for the relative abundance of the corresponding dications formed via charge-stripping in the high-energy collision. [c] Not defined for $n = 1$. [d] A signal corresponding to the $[Ni(DMF)]^{2+}$ dication is observed only at largest sensitivity of the instrument, and its relative abundance is <0.1 relative to the base peak.

and cause diminution of bond energies upon increasing ligation are the repulsive forces between the ligands and the increasingly delocalized charge.[60] At elevated collision energies, the parent ions fragment until the production of $[Ni(DMF)_2]^{2+}$ and $[Ni(DMF)X]^+$, respectively, which show different fragmentation patterns. Let us now analyze this behavior in some more detail for the dicationic species $[Ni(DMF)_n]^{2+}$ and their anion-rebound counterparts $[Ni(DMF)_nX]^+$. Different from most previous studies on solvent-complexes of multiply charged metal ions by means of ESI is the explicit consideration of all steps in ion dissociation by independent ion generation and mass selection of all species discussed below. While the general conclusions do not differ from those derived from CID of multiply solvated polycations at large collision energies, this approach is deemed more adequate as no ambiguities remain in the assignment of the various fragmentation pathways.

$[Ni(DMF)_n]^{2+}$ Dications. As an example for the fragmentation behavior of the multiply solvated dications, the CID breakdown diagram of $[Ni(DMF)_6]^{2+}$ is shown in Figure 2 in which sequential losses of DMF according to reaction 1 are observed ($n + x = 6$).

$$[Ni(DMF)_n]^{2+} \rightarrow [Ni(DMF)_{n-x}]^{2+} + x\mathrm{DMF} \qquad (1)$$

For $n = 6$, loss of the first DMF ligand already occurs at a collision energy nominally set to $E_{CM} = 0$ V, suggesting that the free bond energy of the sixth DMF ligand in the dication is of the magnitude of thermal energy. Loss of the second DMF ligand has an apparent threshold of about 1 eV, and $[Ni(DMF)_3]^{2+}$ appears at about 3.5 eV. At $E_{CM} = 8$ eV, the bisligated dication $[Ni(DMF)_2]^{2+}$ begins to be formed as well. This behavior is nicely consistent with the above deduction that the sequential bond energies increase with decreasing ligation. One reviewer argued, however, that the apparent thresholds might be affected by kinetic shifts in consecutive ion dissociation which would lead to “delayed” thresholds for multiple ligand losses. However, the same trend of increasing bond strengths with decreasing n evolves from the apparent thresholds for loss of a single DMF ligand from mass-selected $[Ni(DMF)_n]^{2+}$ ions generated at variable cone voltages. Thus, the AEs for the loss of one DMF ligand increase from 0.0 ± 0.2 eV for $[Ni(DMF)_6]^{2+}$ to 0.2 ± 0.2 eV for $[Ni(DMF)_5]^{2+}$ and 1.6 ± 0.4 eV for both $[Ni(DMF)_3]^{2+}$ and $[Ni(DMF)_4]^{2+}$. Accordingly, the fifth and the sixth ligands are much more weakly bound to the doubly charged metal cation than the first ones.

The situation changes completely at the stage of $[Ni(DMF)_2]^{2+}$. Thus, not even a trace of a signal corresponding to the $[Ni(DMF)]^{2+}$ dication ($m/z = 65.5$) is observed upon CID. Instead, ligand loss is associated with electron transfer to the metal, thereby affording two singly charged fragments (reaction 2):

$$[Ni(DMF)_2]^{2+} \rightarrow [Ni(DMF)]^+ + DMF^+ \qquad (2)$$

While reaction 2 suggests the formation of equal amounts of $[Ni(DMF)]^+$ and DMF^+, experimentally a clear preference for the former is found (Figure 3). This preference for the detection of heavy fragments in charge-separation reactions can be ascribed to increased scattering of the lighter ion due to the energy released in Coulomb explosion. In this respect, it is quite important that even for the moderate mass difference of $[Ni(DMF)]^+$ ($m/z = 131$) and DMF^+ ($m/z = 73$), the lighter fragment ion is discriminated by a factor of about 6. For larger mass differences, the lighter monocations may therefore in fact be invisible in the experiments. The energy-dependent CID spectra imply an apparent threshold of about 1 eV which is attributed to the energy required to surmount the barrier associated with charge-separation, rather than with the thermochemical threshold of reaction 2. In the course of the charge-separation in reaction 2, nickel is formally reduced to Ni(I) in the product ion $[Ni(DMF)]^+$. Formation of this Ni(I) complex by charge separation of the dicationic species upon successive desolvation is also consistent with an intense signal due to $[Ni(DMF)]^+$ observed in the ESI mass spectra obtained at elevated cone voltages.

To further explore the small dications $[Ni(DMF)_n]^{2+}$ for $n = 1$ and 2, the corresponding monocations were generated by means of chemical ionization in beam-type sector-field mass spectrometer and subjected to charge-stripping (CS) experiments. In CS, a high-energy collision of a mass-selected monocation may lead to the corresponding dication via collisional ionization; of course, fragmentation at the monocationic stage does also take place. In the charge-stripping spectrum of the mass-selected $[Ni(DMF)_2]^+$, a pronounced signal due to the $[Ni(DMF)_2]^{2+}$ dication is observed (Table 1). This finding indicates that this particular dication is quite stable and also accessible by vertical oxidation of the corresponding monocation. In marked contrast, only a very weak signal corresponding to the $[Ni(DMF)]^{2+}$ dication is observed for the monoligated ion; the CS spectrum is instead dominated by monocationic fragments, where the signals due to Ni^+ and DMF^+ show composite peak shapes typical for fragments formed via Coulomb explosion of dications. These observation are in perfect harmony with the electrospray experiments in which only $[Ni(DMF)_2]^{2+}$, but not $[Ni(DMF)]^{2+}$, could be observed.

Notwithstanding, there is an important difference from a methodological point of view. In the ESI experiments, the dications are produced by sequential desolvation of larger ones either in the cone region or upon CID of mass-selected ions. Thus, any $[Ni(DMF)_{n-1}]^{2+}$ dication formed via reaction 1 or a similar process is formed in the presence of another DMF molecule. Upon decreasing stabilization of the dicationic metal center with decreasing *n*, electron transfer from DMF to the metal center becomes more favorable and may in fact prevent dication formation. Consequently, even though some dications exist as well-defined minima in reasonably deep potential-energy wells, they cannot be formed starting from larger entities by means of reaction 1. Here, charge stripping has been shown to offer an alternative approach.[61] Thus, provided that the Franck−Condon factors for vertical ionization from the mono- to the dication are not too unfavorable, the corresponding dication is expected to be formed as long as it exists as bound minima. In the particular case of $[Ni(DMF)_n]^{2+}$, the efficient dication formation for $n = 2$ very much disfavors a particular problem with the Franck−Condon factors for $n = 1$ because for nickel, as for most other transition metals, the binding of the metal ion to the first and the second ligands are similar. Instead, we suggest that the failure to observe the monoligated dication $[Ni(DMF)]^{2+}$ reflects an intrinsic instability of this dication which arises from the fact that the difference of the ionization energies of Ni^+ (18.17 eV) and DMF (9.13 eV) is so large that any minimum possibly formed by coordinative bonding can prevent charge separation according to reaction 3:

$$[Ni(DMF)]^{2+} \rightarrow Ni^+ + DMF^+ \tag{3}$$

$[Ni(DMF)_nX]^+$ Monocations. In addition to the dications, the monovalent counterions X = Cl, Br, and NO_3 also give rise to the corresponding monocations $[Ni(DMF)_nX]^+$ ($n = 1-4$) whose formation can be understood by a rebound of the anion to the dicationic species (reaction 4); in the case of the divalent counterion sulfate, neutral complexes are formed upon anion rebound which remain unobserved in the mass spectrometer.

$$[Ni(DMF)_n]^{2+} + X^- \rightarrow [Ni(DMF)_{n-1}X]^+ + DMF \tag{4}$$

Except for $n = 1$ (see below), exclusive losses of DMF ligands occur upon CID of the mass-selected $[Ni(DMF)_nX]^+$ complexes (reaction 5):

$$[Ni(DMF)_nX]^+ \rightarrow [Ni(DMF)_{n-1}X]^+ + DMF \tag{5}$$

As an example, let us consider the CID breakdown graph of $[Ni(DMF)_4Cl]^+$ (Figure 4). The first DMF ligand is weakly bound and already lost at thermal energy ($E_{CM} = 0$ eV). Evaporation of a second DMF molecule has an apparent threshold of about 1 eV, and the bisligated ion $[Ni(DMF)Cl]^+$ appears about 3 eV. Hence, much as for the dications, the sequential bond strength increases with decreasing *n*. Again, the corresponding experiments conducted with the mass-selected $[Ni(DMF)_nX]^+$ cations fully support this conclusion (data not shown).

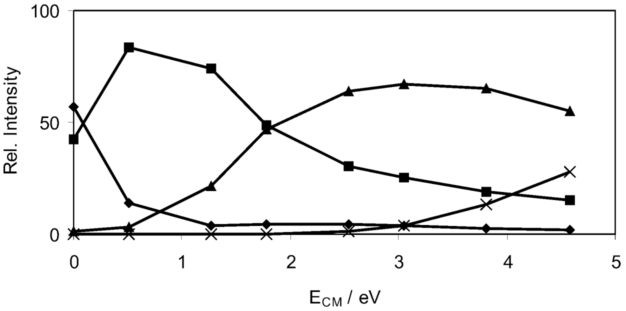

Figure 4. Relative ion intensities as a function of center-of-mass collision energies (E_{CM}) in the CID spectra of $[Ni(DMF)_4Cl]^+$. The symbols are denoted as follows: $[Ni(DMF)_4Cl]^+$ (♦), $[Ni(DMF)_3Cl]^+$ (■), $[Ni(DMF)_2Cl]^+$ (▲), $[Ni(DMF)Cl]^+$ (×).

Much as with the dications, the situation drastically alters for the bisligated species $[Ni(DMF)X]^+$. The dissociation pathway of lowest energy demand for the chloro complex $[Ni(DMF)Cl]^+$ ($m/z = 166$) corresponds to the elimination of hydrogen chloride according to reaction 6a (Figure 5a). Thus, instead of ligand loss, C−H bond activation of DMF does apparently take place. At elevated collision energies (Figures 5b and 5c), one observes evaporation of DMF (reaction 6b) as well as Ni−Cl bond homolysis (reaction 6c) to yield the reduced Ni(I) complex $[Ni(DMF)]^+$. The CID spectra also show fragmentation of the DMF ligand leading to $[NiC_2H_6N]^+$, $[NiC_2H_4N]^+$, as well as $[C_2H_6N]^+$, along with DMF^+, $[C_3H_6NO]^+$, and Ni^+.

$$[Ni(DMF)Cl]^+ \rightarrow [NiC_3H_6NO]^+ + HCl \tag{6a}$$

$$\rightarrow [NiCl]^+ + DMF \tag{6b}$$

$$\rightarrow [Ni(DMF)]^+ + Cl \tag{6c}$$

This energy behavior qualitatively suggests that reaction 6a involves a low-energy rearrangement associated with a considerable kinetic restriction, whereas the direct bond cleavages in reactions 6b and 6c can occur without barriers in excess of the reaction endothermicities. To elucidate which kind of C−H bond is activated in the course of reaction 6a, the corresponding complex of $DC(O)N(CH_3)_2$ (D_1-DMF) was investigated. Upon CID, exclusive loss of HCl is observed for mass-selected $[Ni(D_1\text{-}DMF)Cl]^+$, indicating that bond activation involves one of the *N*-methyl groups rather than the formyl unit.

While identical behavior is observed for the corresponding bromo complex $[Ni(DMF)Br]^+$ ($m/z = 210$), a notable difference occurs for $X = NO_3$. Thus, low-energy CID of mass-selected $[Ni(DMF)NO_3]^+$ leads to the preferential loss of an $NO_2^{\bullet}$ radical concomitant with formation of an ion **1** with $m/z = 147$ for the ^{58}Ni isotope (Figure 6). At increasing collision energies ($E_{CM} > 6$ eV), the reduced complex $[Ni(DMF)]^+$ ($m/z = 131$) as well as $NiNO_3^+$ ($m/z = 120$) are observed, but even then the dominant fragment is **1**. Formally, simple N−O bond cleavage of the nitrate ligand according to reaction 7 would afford the ligated metal-oxide cation $[(DMF)NiO]^+$, structure **A**.

$$[Ni(DMF)NO_3]^+ \rightarrow [(DMF)NiO]^+ + NO_2^{\bullet} \tag{7}$$

The monoxide cations of late 3d transition metals such as nickel are, however, known to be very reactive and are able to activate many substrates several robust substrates.[62,63] Specif-

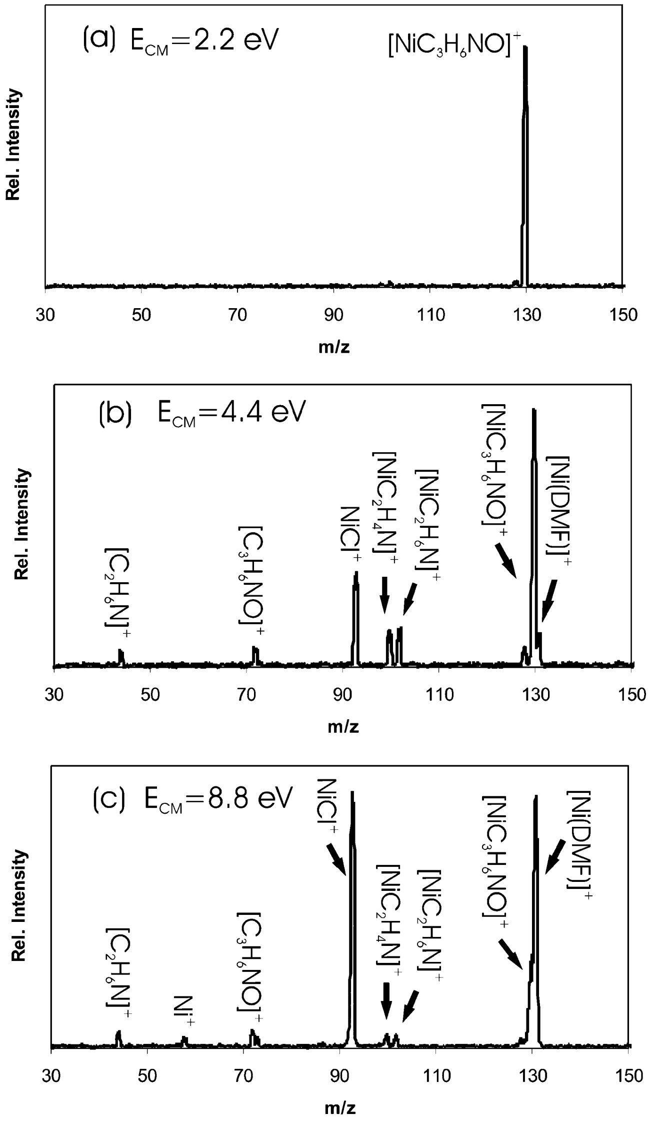

Figure 5. Fragment ions formed upon CID of mass-selected [Ni(DMF)Cl]$^+$ (m/z = 166) at variable collision energies.

ically, bare NiO$^+$ even is capable of activating methane.[64−66] It is therefore quite likely to conceive that also the DMF molecule with considerably more activated C−H bonds is attacked by the coordinated NiO$^+$ unit. Along this line of reasoning, the two primary insertion products [HC(O)N(CH$_3$)CH$_2$−NiOH]$^+$ (**B**) and [(CH$_3$)$_2$NC(O)−NiOH]$^+$ (**C**) appear as conceivable structural alternatives. CID of the mass-selected species **1** (Figure 7) leads to a rich fragmentation pattern and is inconclusive as far as the ion structure is concerned. On one hand, a distinct NiO$^+$ fragment as well as the fragment [Ni(DMF)]$^+$ (m/z = 131) are observed, which would indicate the presence of structure **A**. On the other hand, several signals are observed which indicate the occurrence of oxidation reactions and subsequent rearrangements and may therefore indicate the presence of structures **B** and **C**, e.g., [NiC$_3$H$_5$NO]$^+$ (m/z = 129) due to loss of H$_2$O, [NiC$_2$H$_7$NO]$^+$ (m/z = 119) due to elimination of CO, and [NiC$_2$H$_5$NO]$^+$ (m/z = 117) due to loss of CH$_2$O. Therefore, it appears most likely that species **1** corresponds to a mixture of isomers. A further investigation of the prospects of this “nitrate route” for the possible formation of solvated metal-oxide cations in the gas phase in presently under way, where ligands are considered which are more robust toward oxidation than DMF.

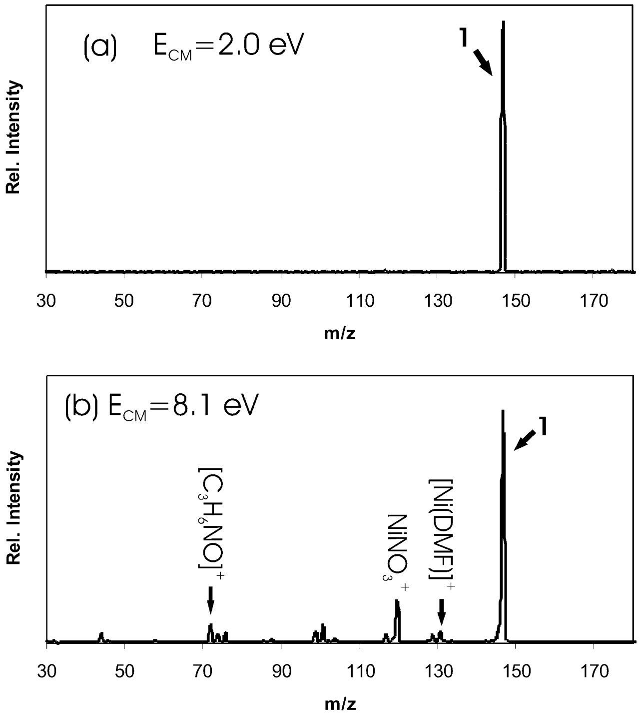

Figure 6. Fragment ions formed upon CID of mass-selected [Ni(DMF)NO$_3$]$^+$ (m/z = 193) at variable collision energies.

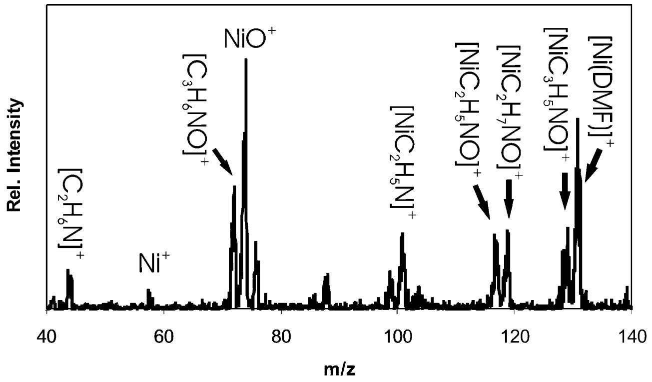

Figure 7. Fragment ions formed upon CID of mass-selected species **1** (m/z = 147) at E_{CM} = 7.1 eV.

Conclusions

Our results demonstrate the ability of nickel(II) ions to create stable complexes in the gas phase with DMF as a ligand. It is obvious that DMF can compete with water for nickel(II), even in water-rich mixtures. The large dipole moment and the strong electron-pair donating capacity of the DMF molecule can account for these observations. Two type of nickel(II) complexes were observed: [Ni(DMF)$_n$]$^{2+}$ with n = 2−6 and [Ni(DMF)$_n$X]$^+$ with n = 1−4 for both 1% w/w DMF and 50% w/w DMF.

The CID spectra of the mass-selected ions show distinct differences between the dissociation pathways of the nickel(II) complexes. Parent ions with a large number of ligands are more fragile, and their fragmentations exclusively lead to evaporation of neutral ligands. Parent ions with a lower number of ligands are more stable toward collisional dissociation. For the bisligated nickel ions species, the single electron-transfer processes are more favorable.[12] Upon CID of the dication [Ni(DMF)$_2$]$^{2+}$, electron transfer from DMF to the metal takes place, forming the reduced complex [Ni(DMF)]$^+$ concomitant with DMF$^+$. The CID spectra of [Ni(DMF)Cl]$^+$ and [Ni(DMF)Br]$^+$ show elimination of HCl and HBr, respectively, at low collision energies and expulsions of atomic halogens concomitant with formation of Ni(I) species at elevated collision energies. In the case of $[Ni(DMF)NO_3]^+$, CID leads to the elimination of NO_2 concomitant with an ionic species for which the solvated nickel-oxide cation $[(DMF)NiO]^+$ is one of several structural alternatives.

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