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Complexation of nickel(II) by ethylenediamine investigated by means of electrospray ionization mass spectrometry

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Abstract

Electrospray ionization (ESI) mass spectrometry is used to investigate the complexation of Ni(II) by ethylenediamine (en) in water/methanol solution of $NiCl_2$, both in the presence and absence of *N*,*N*-dimethylformamide (DMF). The fragmentations of the resulting Ni(II) complexes are studied using collision-induced dissociation (CID) including labeling experiments. The solvated ions formed upon ESI, in the absence of DMF, were: $[Ni(en)_n]^{2+}$ with $n = 2$–5, $[Ni(en)_nCl]^+$ with $n = 1$–3, and the chloro-bridged binuclear ions $[Ni_2(en)_nCl_3]^+$ with $n = 2$–4. The dications $[Ni(en)_n]^{2+}$ show neutral ligand loss, proton transfer between the ligands, and electron transfer from the ligand to Ni(II). CID experiments and comparative studies including related ligands suggest that the multiply solvated dications $[Ni(en)_n]^{2+}$ with $n > 3$ bear a hexacoordinate $[Ni(en)_3]^{2+}$ core with the additional ligands bound via hydrogen bonds. The monocations $[Ni(en)_nCl]^+$ with $n = 2$ and 3 undergo evaporation of ethylenediamine and elimination of HCl. The bisligated monocation $[Ni(en)Cl]^+$ undergoes competing eliminations of HCl and NH_3 at low collision energies, and Ni–Cl bond homolysis at elevated collision energies. The binuclear ions $[Ni_2(en)_nCl_3]^+$ show a loss of neutral $NiCl_2$ leading to the formation of $[Ni(en)_2Cl]^+$. The ions formed upon ESI from solutions which contain DMF as a co-ligand are: $[Ni(en)_3(DMF)_n]^{2+}$ with $n = 0$–4, $[Ni(en)_2(DMF)_n]^{2+}$ with $n = 0$–2, the monocation $[Ni(en)_2(DMF)Cl]^+$ and the binuclear clusters $[Ni_2(en)_nCl_3]^+$ with $n = 2$–4. The mixed solvated Ni(II) ions preferentially eliminate neutral DMF, indicating a favorable coordination of Ni(II) by ethylenediamine.

Keywords: Electrospray ionization; Mass spectrometry; Collision-induced dissociation; Ethylenediamine; Nickel

1. Introduction

Electrospray ionization (ESI), developed by Fenn and co-workers [1–3], is the softest technique available for the transfer of multiply charged metal ion complexes into the gas phase, with almost no fragmentation, directly from solution. This technique, which opened the possibility of analyzing complexes in the absence of solvent, provides important information concerning the structure, stoichiometry, and oxidation state of dissolved metal complexes. Ion production in ESI proceeds via the initial generation of charged droplets, followed by the evaporation of the solvent and the formation of bare or complexed metal ions. During the last years, several groups have successfully used electrospray–ionization mass spectrometry (ESI–MS) for the investigation of the composition, structure, and reactivity of multiply charged transition-metal complexes [4–11].

Polyamines are important industrial chemicals which are used for the production of polymers and plastics [12], and they are important also in biochemistry because they are present in the cells of microorganisms and animal organisms and contribute to the stabilization of the structure and activity of *t*RNA and DNA [13]. Ethylenediamine as the most simple of polyamines behaves as a bidentate ligand that can form two coordinative bonds with a metal atom through the lone pair electrons on both nitrogens [14]. The coordination of ethylenediamine to a metal ion leads to a five-membered chelate ring with many of the stereochemical characteristics of cyclopentane [15,16]. Transition-metal cations generally show higher affinities to ethylenediamine in comparison with alkaline earth and alkali metal cations [17]. Ethylenediamine is a stronger base than ammonia ($K_d = 8.5 \times 10^{-5}$) even though it has physicochemical properties comparable with ammonia, such as dipole moment, dielec-

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tric constant, and surface tension [18]. Therefore, it is frequently present as a partially or fully protonated ligand (dependent on pH) which may interact with anions to form complexes [17]. Furthermore, ethylenediamine has a large value of pK_s (15.3/25 °C) indicating that the autoprotolysis reaction 2en $\rightleftharpoons$ (en)H^+ + (en-H)$^-$, takes place to a low extent [19]. Investigations of the conformational energy and the structural stability of ethylenediamine by ab initio methods show that the two most stable conformations are stabilized by intramolecular hydrogen bonding (N–H $\cdots$ N) with stabilization energies up to 20 kcal mol^{-1} [20,21]. In aqueous solutions, ethylenediamine interacts strongly with water molecules through hydrogen bonds, therefore, the mixtures exhibit negative deviations from ideality [22,23]. It has been found that the non-polar group –CH_2CH_2– does not exhibit a notable hydrophobic effect [24].

Since the Ni(II) ion plays a major role in biological and geochemical processes, it has received much attention and investigation over the last few years. Divalent nickel (d^8 configuration) forms a large number of complexes encompassing all the common geometries, octahedral (6-coordinate), trigonal bipyramidal (5), square pyramidal (5), tetrahedral (4), and square planar (4). Although some complexes of Ni(III) are stable in the solid state and in solution of several organic media [25,26], Ni(II) is the most important oxidation state in the aqueous and non-aqueous chemistry of nickel [27]. Ni(II) has an extensive aqueous chemistry based on the complex $[Ni(H_2O)_6]^{2+}$ which is always formed in the absence of strongly interacting ligands. Addition of *N*-donor ligands, such ethylenediamine (en), leads to sequential replacement of the coordinated water molecules and to the formation of mono, bis, and trisligated dications of the general form $[Ni(en)_n]^{2+}$ ($n = 1$–3). According to Watkins and Vigee [28], the $[Ni(en)_n]^{2+}$ complexes are essentially non-dissociating even in the presence of polar solvents such as dimethylsulfoxide (DMSO).

Several researchers have investigated Ni(II) complexes of ethylenediamine, *N*-alkyl-ethylenediamines, *N*,*N*′-dialkyl-ethylenediamines, and *C*-substituted ethylenediamines in the condensed phase [29–34]. The interest was focused on the examination of the effects of the substituents on the stabilities of the complexes as well as the determination of magnetic properties of the complexes formed.

The purpose of this paper is the investigation of the complexation of Ni(II) by ethylenediamine in water/methanol solution using ESI–MS, both in the presence and absence of *N*,*N*-dimethylformamide (DMF) as a co-ligand which we have investigated before [35]. In this context, three aspects in the chemical behavior of ligated $[NiL_n]^{2+}$ ions are of particular interest: (i) at which number of ligands n, bond activations or electron transfer reactions occur in the dissociation of the Ni(II) complexes, (ii) what are the bonding patterns of those multiply ligated species which formally exceed the hexafold coordination of nickel, and (iii) to which extent can DMF compete with ethylenediamine as a ligand.

2. Experimental section

All 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) [36]. For each ion of interest the instrument parameters were optimized for maximum ion abundances. Typical adjustments were: capillary voltage 3.6 kV, HV lens (counter electrode) 30 V, cone voltage 0–80 V, RF lens 0.1 V, skimmer 1.0 V, and skimmer-lens offset 5 V. In the experiments, mmolar solutions of $NiCl_2$ in a 1:1 water/methanol mixture which contains: (a) 1.0% (w/w) ethylenediamine, (b) equal amounts of ethylenediamine and DMF (1% w/w) 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 range examined in this study was usually 30–1000 (*m*/*z*). All mass-to-charge ratios (*m*/*z*) given below refer to the most abundant ^{58}Ni isotope.

Collision-induced dissociation (CID) experiments were performed with xenon at various collision energies ($E_{\mathrm{Lab}} =$ 0–25 eV). The collision gas pressure was approximately 3×10^{-4} mbar. 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 BIO-Q does not allow to directly extract quantitative threshold information from CID experiments due to several limitations of the commercial instrument [36]. Even at $E_{\mathrm{Lab}} = 0$ eV, for example, non-negligible ion decay is observed for weakly bound ions which is in part attributed to the presence of collision gas not only in the hexapole, but also in the focusing regions between the mass analyzers. However, the CID spectra show distinct dependences from the collision energies applied which provide some semi-quantitative information about the energetics of the ions examined. In a strict sense, the limitations of the instrument would, therefore, require to display all spectra at various collision energies, if the trends evolving from comparison of energy-dependent CID spectra of different ions are to be discussed. To avoid such an exhaustive display of raw data, the threshold behaviors were analyzed in an empirical manner by fitting sigmoid functions of the type $I_i(E_{\mathrm{CM}}) = (\mathrm{BR}_i/(1 + \mathrm{e}^{(E_{1/2}-E_{\mathrm{CM}})^b})$ to the observed relative fragment ion yields using a least-square criterion; for the parent ion M the equation holds: $I_M(E_{\mathrm{CM}}) = [1 - \sum(\mathrm{BR}_i/(1 + \mathrm{e}^{(E_{1/2,i}-E_{\mathrm{CM}})b_i}))]$ [37]. Here, BR_i stands for the branching ratio of a particular product ion ($\sum \mathrm{BR}_i = 1$), $E_{1/2}$ is the energy at which the sigmoid function has reached half of its maximum, and b describes the rise of the sigmoid curve. In consecutive dissociations, all secondary product ions were summed to the primary fragment. Further, non-negligible ion decay at $E_{\mathrm{Lab}} = 0$ V as well as some fraction of non-fragmenting parent ions at large collision energies (due to the single collision conditions maintained) were acknowledged by means of scaling and normalization. This empirical, but physically reasonable, approach is able to reproduce the measured ion yields quite well. It is important to note, however, that the term $E_{1/2}$ used in the exponent does not correspond to the intrinsic appearance energies (AE) of the respective fragmentations, not to speak of the corresponding thermochemical thresholds at 0 K. The phenomenological AEs given below were derived from linear extrapolations of the rise of the sigmoid curves at $E_{1/2}$ to the base line. In addition, some ion/molecule reactions of $[\mathrm{Ni(en)}_n]^{2+}$ with $n = 3$–5 with neutral DMF were examined. To this end, the dication complexes were mass-selected using Q1 and then interacted with neutral DMF leaked into the hexapole at a collision energy nominally set to 0 eV. In order to be able to observe also sequential ligand-exchange reactions, the pressure of neutral DMF was adjusted such that multiple collisions in the hexapole can occur.

Ethylenediamine (Fluka, > 99.9%), *N*,*N*-dimethylformamide (Merck, 99.9%), methanol (Merck, > 99.9%) were spectral grade, and the water was doubly distilled. Nickel chloride hexahydrate (Fluka, p.a. > 98.0%) was used without further purification.

3. Results and discussion

3.1. Characterization and fragmentation of Ni(II)–ethylenediamine complexes

ESI of $\mathrm{NiCl_2}$ dissolved in water/methanol mixtures containing 1% ethylenediamine leads to the following nickel-containing cations: the dications $[\mathrm{Ni(en)}_n]^{2+}$ with $n = 2$–5, the monocations $[\mathrm{Ni(en)}_n\mathrm{Cl}]^+$ with $n = 1$–3, and the binuclear monocations $[\mathrm{Ni_2(en)}_n\mathrm{Cl_3}]^+$ with $n = 2$–4. The relative intensities of the dications are considerably lower than those of the monocations, and the yield of dinuclear complexes increases with nickel concentration, as expected. In addition, the Brønsted basicity of ethylenediamine is reflected by the presence of signals at $m/z = 61$, 121, and 181, which correspond to proton-bound oligomers of ethylenediamine, $\mathrm{(en)}_n\mathrm{H}^+$ with $n = 1$–3. For all species, the number of ligands n of the solvated ions formed and, thus, the extent of solvation depends on the cone voltage (U_C) in the ESI source which crucially determines the softness or hardness of the ionization conditions. At low U_C, multiply ligated ions prevail, whereas ligation drops with rising U_C, and further increase of U_C causes fragmentation of the solvent molecules as well as electron transfer from ethylenediamine to the metal concomitant with a reduction from Ni(II) to Ni(I).

3.2. $[\mathrm{Ni(en)}_n]^{2+}$ dications

The CID spectra of the mass-selected dications $[\mathrm{Ni(en)}_n]^{2+}$ with $n = 3$–5 show evaporation of neutral ethylenediamine ligands according to reaction 1 as dominant pathway.

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

The largest number of sequential ethylenediamine losses was three for $n = 5$, two for $n = 4$, and one for $n = 3$. Ligand losses are common in the dissociation of metal dication complexes with more than two ligands [38,39]. At the stage of $[\mathrm{Ni(en)_2}]^{2+}$, the ethylenediamine elimination decreases sharply and intracomplex electron transfer followed by charge separation according to reaction 2a becomes more probable.

$$[\mathrm{Ni(en)_2}]^{2+} \rightarrow [\mathrm{Ni(en)}]^{+} + \mathrm{en}^{+} \qquad (2a)$$

$$[\mathrm{Ni(en)_2}]^{2+} \rightarrow [\mathrm{Ni(en)}]^{2+} + \mathrm{en} \qquad (2b)$$

Occurrence of electron transfer can be rationalized by the fact that the ionization energy (IE) of ethylenediamine (7.6 eV) is much lower than the ionization energy of Ni^+ (18.2 eV); a difference for which bonding of the remaining ligand to Ni(II) cannot compensate. The failure to observe the monoligated $[\mathrm{Ni(en)}]^{2+}$ dication ($m/z = 59$) via evaporation of neutral ethylenediamine (reaction 2b) implies that this complex is not attainable under these conditions. It is not justified, however, to interpret the absence of the $[\mathrm{Ni(en)}]^{2+}$ dication upon CID of $[\mathrm{Ni(en)_2}]^{2+}$ as an indication for the intrinsic instability of the monoligated dication $[\mathrm{Ni(en)}]^{2+}$ with respect to the charge separation asymptote $\mathrm{Ni}^+ + \mathrm{en}^+$. As the IE of the ligand is low, efficient and facile electron transfer from the neutral ligand to the metal dication is likely to suppress the formation of the monoligated dication in favor of the corresponding monocation (for $\mathrm{Cu(H_2O)}^{2+}$ as a prominent example in this respect, see [40]).

The large difference between the ionization energies of Ni^+ and ethylenediamine also leads to a tendency for charge reduction by interligand proton transfer.[1] Thus, for the dications with $n = 3$–5, in competition with ligand losses, proton transfer between ethylenediamine ligands is observed as well, leading to the formation of $[\mathrm{Ni(en)(en\text{-}H)}]^+$ ($m/z = 177$). The charge-reduced ion $[\mathrm{Ni(en)(en\text{-}H)}]^+$ could originate from the dications $[\mathrm{Ni(en)_3}]^{2+}$ and/or $[\mathrm{Ni(en)_4}]^{2+}$, depending on whether the complementary fragment is $\mathrm{(en)H}^+$ or $\mathrm{(en)_2H}^+$, respectively. However, the protonated monomer $\mathrm{(en)H}^+$ ($m/z = 61$) which appears in the CID spectra confirms that the charge-reduced product most likely arises from $[\mathrm{Ni(en)_3}]^{2+}$ according to reaction 3.

$$[\mathrm{Ni(en)_3}]^{2+} \rightarrow [\mathrm{Ni(en)(en\text{-}H)}]^{+} + \mathrm{(en)H}^{+} \qquad (3)$$

CID experiments using deuterated ethylenediamine ($\mathrm{D_2NCH_2CH_2ND_2}$) reveal that the proton lost originates

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[1] A reviewer correctly remarked that there is no direct correlation between the IE and the PA of a ligand L. In a thermochemical cycle, both quantities are related as $\mathrm{PA(L)} = \mathrm{IE(H)}\text{-}\mathrm{IE(L)} + \mathrm{D(L^+\text{-}H)}$ where $\mathrm{D(L^+\text{-}H)}$ stands for the hydrogen-atom affinity of the ionized ligand. For typical closed-shell organic ligands, however, a rough correlation exists in that ligands with low IEs have high PAs and vice versa.

from one of the amino groups. According to Blades et al., proton transfer is a common process for protic ligands such as ethylenediamine, while for aprotic ligands such as DMF or DMSO, charge-transfer processes often predominate [41]. Our previous results concerning the dications $[Ni(DMF)_n]^{2+}$, for which only electron transfer from DMF to Ni(II) has been observed [35], support these conclusions. Beyer et al. [42] suggested “salt-bridge structures” of the form $M(II)–OH^{-}–H_3O^{+}$ in the transition state of proton transfer in hydrated alkaline earth dications, which lower the activation barrier for the proton migration. According to their theoretical studies, electron transfer is by and large suppressed if proton transfer can take place [43]. Similar “salt-bridge” mechanisms may play a role in proton transfer reactions observed for other solvated metal ions as well. For example, Shvartsburg [44] demonstrated the occurrence of interligand proton transfer for several trications complexed by 4-hydroxy-4-methyl-2-pentanone. Kohler and Leary [45] observed this pathway in some dications complexed by acetonitrile. Another example was given by Seto and Stone [46] for Cu(II) complexed by amino acids.

As an example for the fragmentation behavior of the multiply solvated dications, selected CID spectra of $[Ni(en)_5]^{2+}$ are shown in Fig. 1. At low collision energy ($E_{CM} = 0.5$ eV, Fig. 1a), the spectrum is dominated by signals corresponding to successive evaporation of ethylenediamine. The interligand proton transfer process, followed by charge separation, becomes more pronounced at $E_{CM} = 3.2$ eV (Fig. 1b). At increased collision energy ($E_{CM} = 4.3$ eV, Fig. 1c), the spectrum reveals a peak which corresponds to bisligated $[Ni(en)_2]^{2+}$ ($m/z = 89$). Identical conclusions evolve from the CID spectra of dications with $n = 3$ and 4 (data not shown). As mentioned above, an exception is $n = 2$, for which collision-induced fragmentation to the reduced $[Ni(en)]^{+}$ monocation is observed exclusively (reaction 2a).

The formation of the multiply ligated dications $[Ni(en)_n]^{2+}$ with $n > 3$ in the mass spectrometric experiments requires some additional consideration because these complexes are known not to be present in solution [34], as they exceed the formal coordination number of six for the nickel atom. Two alternative explanations can be put forward in this respect. At first, ethylenediamine may also act as a monodentate ligand in the gas phase, even if it traditionally serves as a bidentate ligand in the condensed phase. An explanation of this phenomenon has been proposed by Wright and co-workers [47,48]. If one end of ethylenediamine becomes attached to the cationic metal core, the positive charge on the Ni(II) center polarizes the ligand leading to a δ^{+} charge at the unattached function of the ligand, which hence, is repelled as it approaches the metal cation. It has been also suggested that the unfavorable change in entropy associated with the formation of a chelate complex affects to a notable degree the interactions between ethylenediamine and metal ions in the gas phase[47]. Along this line of reasoning, the $[Ni(en)_n]^{2+}$ complexes with $n > 3$ would, therefore, maintain six-fold coordination of the metal atom with some of the en ligands only bound by one of the two amino groups. Alternatively, however, the well-known ability of ethylenediamine to form hydrogen bonds may assist the formation of a second solvation shell with hydrogen-bonded ligands. For the system $[Ni(en)_n]^{2+}$ itself, this question cannot be addressed unequivocally by the present experiments. Upon CID, for example, one would expect facile losses of the first en ligands for both types of coordination as is indeed observed experimentally. Thus, ligand-loss form the outer sphere is anyhow expected to be facile and expulsion of one en unit acting as a monodentate ligand can be assisted by recoil of a second ligand to the metal center. In order to further address this intriguing question, dicationic complexes $[NiL_n]^{2+}$ with some related ligands L were probed in a few additional experiments. As structurally related ligands L, we have chosen *N,N,N,N*-tetramethyl ethylene diamine

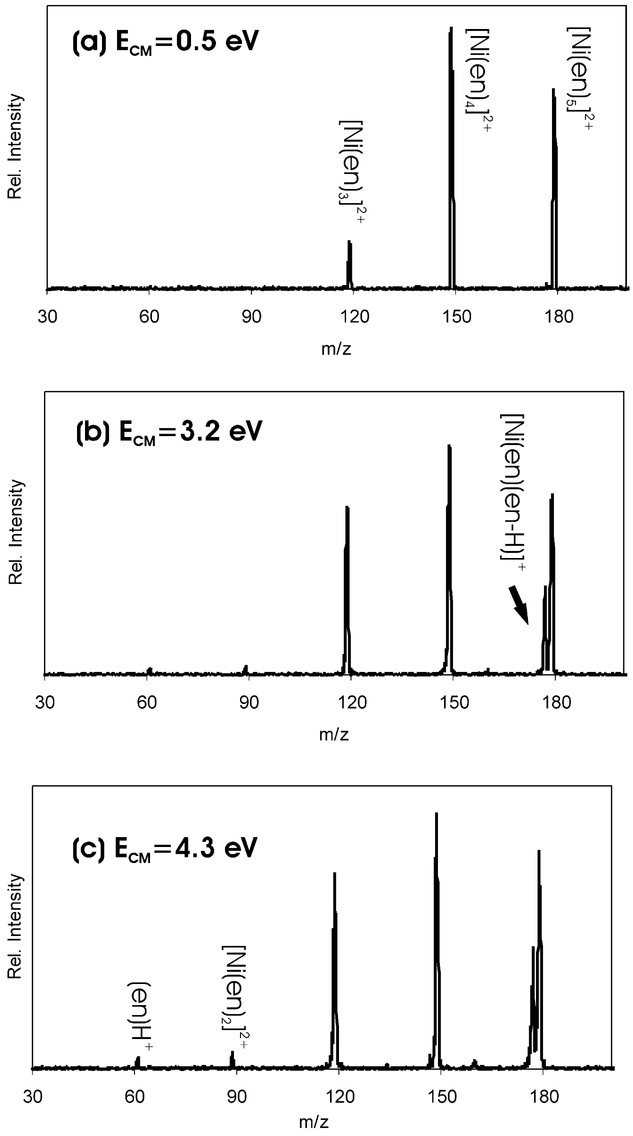

Fig. 1. CID spectra of mass-selected $[Ni(en)_5]^{2+}$ ($m/z = 179$) at variable collision energies (E_{CM}).

(TMEDA), dimethoxy ethane (DME), and ethylene glycol (EG). While all of them are bidendate, due to permethylation of the functional groups TMEDA and DME cannot form hydrogen bonds, whereas, glycol should behave similar to ethylene diamine. Upon ESI of nickel(II) solutions in methanol/water, some interesting observations corroborate this conjuncture. Here, we exclusively focus on the multiply coordinated dication complexes formed under gentle ionization conditions. In the presence of TMEDA, a pronounced signal due to $Ni(L)_3^{2+}$ is observed while dications with $n > 3$ are absent. Likewise, no $Ni(L)_n^{2+}$ dications with $n > 3$ are formed with DME. Interestingly, however, mixed complexes of the type $[Ni(DME)_n(H_2O)_m]^{2+}$ are observed under soft spray conditions, for example, $[Ni(DME)_4(H_2O)_m]^{2+}$ with $m = 1$–3 and $[Ni(DME)_5(H_2O)_m]^{2+}$ with $m = 2$–4. Upon CID of mass-selected $[Ni(DME)_5(H_2O)_4]^{2+}$, consecutive losses of H_2O and DME ligands are observed converging to $Ni(DME)_3^{2+}$, but most decisively, the pure DME-complex $Ni(DME)_4^{2+}$ is not observed as a fragment. Likewise, CID of mass-selected $[Ni(DME)_4(H_2O)_2]^{2+}$ leads to $[Ni(DME)_4(H_2O)]^{2+}$, $[Ni(DME)_3(H_2O)_2]^{2+}$, $[Ni(DME)_3(H_2O)]^{2+}$, and $Ni(DME)_3^{2+}$, but only a negligible fraction of $Ni(DME)_4^{2+}$ is formed. In marked contrast, ethylene glycol behaves similar to ethylene diamine in that multiply ligated complexes such as $Ni(EG)_n^{2+}$ with $n = 4$–6 are observed at low cone voltages. Resuming these observations, we conclude that the formation of multiply ligated dications which exceed the formal coordination number of six crucially depends on the ability of the bifunctional ligand to form hydrogen bonds. Thus, the permethylated ligands TMEDA and DME can only form larger dicationic complexes in the presence of additional water molecules which, in turn, provides a network of hydrogen bonds. Accordingly, the option mentioned above that ethylenediamine may act as a monodentate ligand in $[Ni(en)_n]^{2+}$ with $n > 3$ is discarded in favor of hydrogen bonding in terms of incorporating some of the ligands in second solvation shell.

As an additional probe, mass-selected $[Ni(en)_n]^{2+}$ dications were reacted with neutral DMF in the hexapole under quasi-thermal conditions, that is, E_{CM} set to nominally 0 eV. To this end, multiple collisions with DMF were allowed, thereby, permitting the occurrence of consecutive ion/molecule reactions. The case of $[Ni(en)_3]^{2+}$ serves as a reference as we may safely assume a hexacoordinate structure with three ethylendiamine units as bidentate ligands for this dicationic complex. Upon reaction with DMF, association of one DMF molecule as well as charge separation preceded by intraligand proton transfer are observed (reactions 4a and 4b).

$$[Ni(en)_3]^{2+} + DMF \rightarrow [Ni(en)_3(DMF)]^{2+} \tag{4a}$$

$$[Ni(en)_3]^{2+} + DMF \rightarrow [Ni(en)(en\text{-}H)]^{+} + (en)H(DMF)^{+} \tag{4b}$$

In a subsequent step, the $[Ni(en)_3(DMF)]^{2+}$ dication formed in reaction (4a) undergoes exchange of one en ligand against DMF to afford $[Ni(en)_2(DMF)_2]^{2+}$; a direct exchange of en in $[Ni(en)_3]^{2+}$ by DMF to afford $[Ni(en)_2(DMF)]^{2+}$ is not observed, however. In marked contrast, the dication $[Ni(en)_4]^{2+}$ rapidly exchanges one and $[Ni(en)_5]^{2+}$ exchanges two en ligands against DMF (reactions 5–7), whereas, further exchanges as well as association reactions are slow.

$$[Ni(en)_4]^{2+} + DMF \rightarrow [Ni(en)_3(DMF)]^{2+} + en \tag{5}$$

$$[Ni(en)_5]^{2+} + DMF \rightarrow [Ni(en)_4(DMF)]^{2+} + en \tag{6}$$

$$[Ni(en)_4(DMF)]^{2+} + DMF \rightarrow [Ni(en)_3(DMF)_2]^{2+} + en \tag{7}$$

This behavior is fully consistent with the description of the $[Ni(en)_n]^{2+}$ species with $n > 3$ as ions having a hexacoordinate nickel(II) $[Ni(en)_3]^{2+}$ core with additional en ligands bound via hydrogen bonds which undergo facile exchange in the presence of a competing ligand such as neutral DMF. As an example, the spectrum showing the reaction of the mass-selected $[Ni(en)_5]^{2+}$ with DMF is given in Fig. 2.

3.3. $[Ni(en)_nCl]^+$ monocations

Much like for the dications, the dominant process observed upon CID of the monocations $[Ni(en)_nCl]^+$ with $n = 2$ and 3 corresponds to the evaporation of neutral ligands (reaction 8).

$$[Ni(en)_nCl]^+ \rightarrow [Ni(en)_{n-x}Cl]^+ + x\,en \tag{8}$$

$$[Ni(en)_2Cl]^+ \rightarrow [Ni(en)(en\text{-}H)]^+ + HCl \tag{9}$$

As mentioned above, the desolvation process is far more facile for complexes with a large number of ligands. In all instances, the parent ions continue to lose ligands until the fragment $[Ni(en)Cl]^+$ ($m/z = 153$) is formed, which appears to be a particularly stable complex (see below). Another dissociation process observed for $n = 2$ and 3 corresponds to the elimination of HCl (reaction 9), leading to the formation

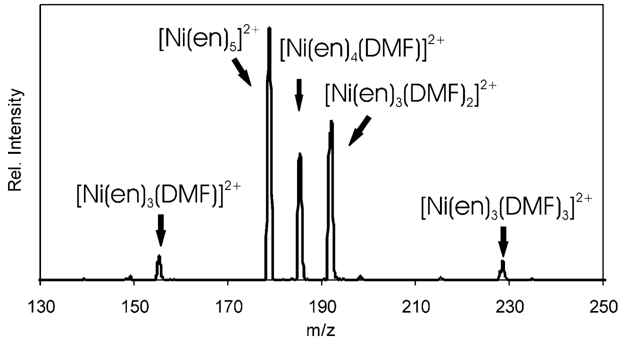

Fig. 2. Mass spectrum resulting from the ion–molecule reaction of mass-selected $[Ni(en)_5]^{2+}$ with DMF; for details, see text.

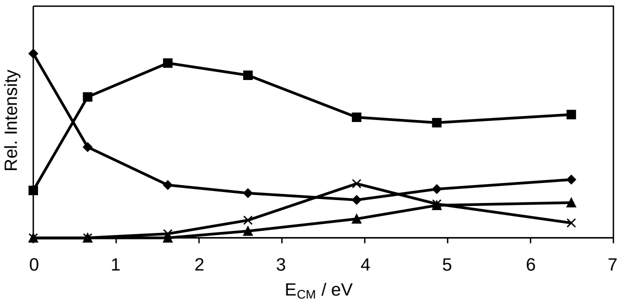

Fig. 3. Relative ion intensities as a function of center-of-mass collision energies (ECM) in the CID spectra of $[Ni(en)_3Cl]^+$. The symbols are denoted as follows: $[Ni(en)_3Cl]^+$ (◆), $[Ni(en)_2Cl]^+$ (■), $[Ni(en)Cl]^+$ (▲), $[Ni(en)(en\text{-}H)]^+$ (×).

of $[Ni(en)(en\text{-}H)]^+$ with $m/z = 177$. Deuterium labeling experiments demonstrate that the hydrogens of the amino groups are involved in reaction 9, that is, exclusive loss of DCl occurs when $D_2NCH_2CH_2ND_2$ is used as a ligand.

As an example, the breakdown diagram of $[Ni(en)_3Cl]^+$ is discussed in more detail. As shown in Fig. 3, the first ethylenediamine ligand is weakly bound and already lost at thermal energy ($E_{CM} = 0$ eV). The bisligated ion $[Ni(en)Cl]^+$ ($m/z = 153$) appears about $E_{CM} = 2.6$ eV. This behavior is consistent with the previous conclusion that the interactions between a metal ion and a ligand become stronger with decreasing ligation [49,50]. The elimination of HCl has an apparent threshold of about 1.6 eV. Similar conclusions and relative threshold differences can be extracted from the fragmentation of $[Ni(en)_2Cl]^+$ (data not shown), thereby, justifying the consideration of multiple CID as a first-order approximation.

The dissociation pathways of the mass-selected $[Ni(en)Cl]^+$ monocation are quite different from that of the multiply ligated chloro complexes and strongly depend on the collision energy. At a collision energy of about 4 eV, elimination of hydrogen chloride (reaction 10a) takes place yielding the fragment $[Ni(en\text{-}H)]^+$ ($m/z = 117$). Deuterium labeling shows that the proton originates from the amino groups. In competition, C–N bond activation of ethylenediamine occurs yielding the fragment $[Ni(en\text{-}NH_3)Cl]^+$ ($m/z = 136$) via elimination of ammonia (reaction 10b), and only ND_3 is lost when $D_2NCH_2CH_2ND_2$ is used as a ligand. At elevated collision energies ($E_{CM} > 9$ eV), Ni–Cl bond homolysis (reaction 10c) to yield the complex $[Ni(en)]^+$ ($m/z = 118$) as well as elimination of neutral ethylenediamine (reaction 10d) to yield diatomic $NiCl^+$ ($m/z = 93$) are observed. This energy behavior strongly suggests that the activation energies associated with the rearrangement involved in the eliminations of HCl (reaction 10a) and NH_3 (reaction 10b) are lower than those of $Cl^\bullet$ loss (reaction 10c) as well as the evaporation of the en ligand (reaction 10d).

$$[Ni(en)Cl]^+ \rightarrow [Ni(en\text{-}H)]^+ + HCl \quad (10a)$$

$$[Ni(en)Cl]^+ \rightarrow [Ni(en\text{-}NH_3)Cl]^+ + NH_3 \quad (10b)$$

$$[Ni(en)Cl]^+ \rightarrow [Ni(en)]^+ + Cl^\bullet \quad (10c)$$

$$[Ni(en)Cl]^+ \rightarrow NiCl^+ + en \quad (10d)$$

We note in passing that these findings strongly support the proposed ion structures compared to possible isomeric variants. Occurrence of reactions 10c and 10d at elevated collision energies strongly suggests that the mass-selected ions correspond to $[Ni(en)Cl]^+$ because the formation of the fragments $[Ni(en)]^+$ and $NiCl^+$ upon CID implies that these units are present in the complexes. Losses of HCl and NH_3 indicate, however, that some isomerization occurs either in the ionization process, for example, formation of the complex $[(HCl)Ni(en\text{-}H)]^+$ rather than $[Ni(en)Cl]^+$, or more likely, upon CID.

3.4. $[Ni_2(en)_nCl_3]^+$ clusters

The tendency of Ni(II) to form polynuclear complexes is revealed by the observation of the binuclear monocations $[Ni_2(en)_nCl_3]^+$ ($n = 2$–4). Not surprisingly, the relative yields of the binuclear cations increase with the Ni(II) concentration in solution. While the structure of the binuclear monocations $[Ni_2(en)_nCl_3]^+$ in the gas phase is unknown, failure to observe the corresponding binuclear complexes when $Ni(NO_3)_2$ is used as a Ni(II) source in the ESI experiments, suggests that the Ni(II) ions are bridged by Cl^- and not by ethylenediamine. Chloro-bridges with two equivalent chlorine atoms between the two metal ions are well-known in coordination chemistry. Thus, the most logical assignment is that the two Ni(II) centers are bridged by two chlorine groups [51,52]. The binuclear ions $[Ni_2(en)_nCl_3]^+$ may either be generated from the monocations $[Ni(en)_nCl]^+$ upon increasing metal concentration in the droplets during evaporation of the solvent molecules or the cluster formation may reflect some degree of aggregation already occurring in solution.

$$[Ni_2(en)_nCl_3]^+ \rightarrow [Ni_2(en)_{n-x}Cl_3]^+ + x\,en \quad (11)$$

$$[Ni_2(en)_2Cl_3]^+ \rightarrow [Ni(en)_2Cl]^+ + NiCl_2 \quad (12)$$

Upon CID of mass-selected $[Ni_2(en)_nCl_3]^+$ complexes, elimination of ethylenediamine according to reaction 11 is observed; as an example, two CID spectra of $[Ni_2(en)_4Cl_3]^+$ are shown in Fig. 4. At the stage of $[Ni_2(en)_2Cl_3]^+$, however, cleavage of the Ni–Cl–Ni bridge leads to loss of a $NiCl_2$ moiety, concomitant with formation of the ionic fragment $[Ni(en)_2Cl]^+$ in reaction 12. Hence, degradation of the binuclear cluster is preferred over further losses of ligands for $n = 2$; similar expulsions of neutral metal halides have been observed for $Fe_2Cl_n{}^+$ and $Si_2Cl_n{}^+$ cations [53,54]. In conjunction with the above arguments about chloro-bridged nickel clusters, a plausible structure of the dinuclear cluster with $n = 2$ would be $[(en)_2Ni(\mu\text{-}Cl)_2NiCl]^+$ with the two nickel atoms bearing different coordination motifs: the charge-carrying nickel is stabilized by the en ligands,

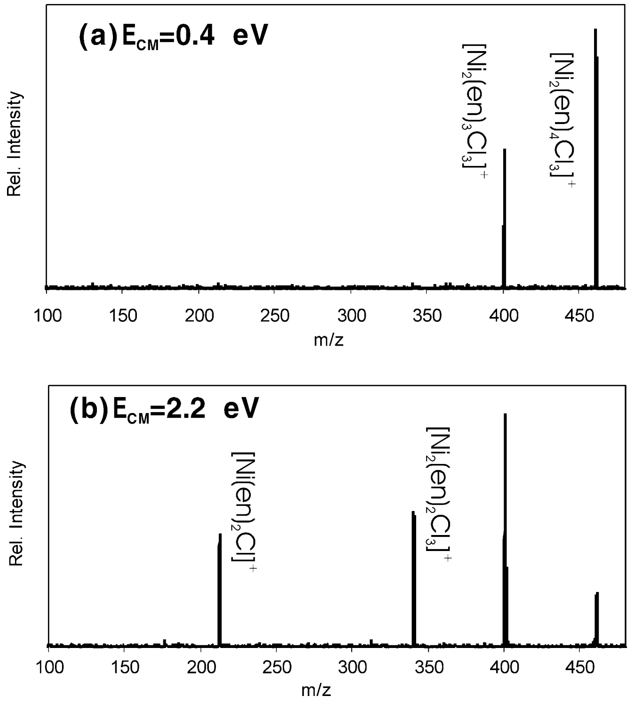

Fig. 4. CID spectra of mass-selected $[Ni_2(en)_4Cl_3]^+$ (m/z = 461) at variable collision energies (E_{CM}).

whereas, the formally neutral nickel atom is coordinated to chlorine only.

3.5. *Mixed complexes of Ni(II) with ethylenediamine and DMF*

The second part of this study deals with the competition between ethylenediamine and DMF for ligation of Ni(II). Therefore, dilute solutions of $NiCl_2$ in water/methanol which contain equal amounts of ethylenediamine and DMF (1% w/w) were investigated by ESI–MS. It is well-known that the preferential solvation in mixed solvents results from both specific and non-specific interactions between the metal ion and the solvent. It is to be expected that the differences in the nature of the ethylenediamine and DMF ligands influence the type of the formed mixed-ligand Ni(II) complexes and CID of mass-selected ions may serve to probe to which extent this holds true for the fragmentation pathways of these complexes.

The ESI mass spectra recorded at variable cone voltages reveal the formation of the following mixed-ligand Ni(II) complexes: the dications $[Ni(en)_3(DMF)_n]^{2+}$ with $n = 1$–4, $[Ni(en)_2(DMF)_n]^{2+}$ with $n = 1$–2, and the monocation $[Ni(en)_2(DMF)Cl]^+$. In addition, clusters which contain exclusively ethylenediamine are observed, $[Ni_2(en)_nCl_3]^+$ with $n = 2$–4. The presence of the cations $[Ni_2(en)_nCl_3]^+$ on the one hand, and the lack of complexes which contain only DMF on the other hand indicate a preferential ligation of Ni(II) by ethylenediamine.

The CID spectra of the dications $[Ni(en)_3(DMF)_n]^{2+}$ (n = 1–4) are governed by sequential losses of neutral DMF (reaction 13) with formation of $[Ni(en)_3]^{2+}$ as the terminus prior to further degradation of the pure ethylenediamine complex (see above).

$$[Ni(en)_3(DMF)_n]^{2+} \rightarrow [Ni(en)_3(DMF)_{n-x}]^{2+} + x\,DMF \tag{13}$$

The trend of the dications for preferential evaporation of neutral DMF ligands demonstrates that Ni(II) has a significantly larger affinity for the amino group of ethylenediamine than for the carbonyl oxygen of DMF. Furthermore, the DMF ligands appear to be bound to the outer sphere of a $[Ni(en)_3]^{2+}$ core. The higher stability of the Ni(II)–ethylenediamine complexes compared to Ni(II)–DMF can be attributed to the chelating effect of ethylenediamine [55,56].

A second dissociation process observed at elevated collision energies leads to the formation of the solvated ions $[Ni(en)_2(DMF)_n]^{2+}$ (n = 0–2) resulting from the fragmentation of $[Ni(en)_3(DMF)_n]^{2+}$ (n = 0–2) by the loss of neutral ethylenediamine. This observation parallels the substitution of one en ligand by two DMF units in the ion/molecule reactions of $[Ni(en)_n]^{2+}$ with neutral DMF (see above). In addition, the CID spectra of all the dications show weak peaks at m/z = 61, 74, and 134 which are assigned to the protonated species $(en)H^+$, $(DMF)H^+$, and $(en)(DMF)H^+$, respectively, formed concomitantly with hydrogen-transfer and charge separation leading to $[Ni(en)(en\text{-}H)]^+$.

As an example for the dissociation of the mixed complexes, two selected CID spectra of $[Ni(en)_3(DMF)_4]^{2+}$ are given in Fig. 5. At low collision energy (E_{CM} = 0.4 eV, Fig. 5a), the spectrum shows only peaks corresponding to losses of DMF. The apparent threshold for the removal of the last DMF ligand and the formation of $[Ni(en)_3]^{2+}$ is quite small (∼1 eV), which confirms the notion that the interactions between Ni(II) and DMF are relatively weak. At higher collision energy (E_{CM} = 3.0 eV, Fig. 5b), the spectrum also reveals the formation of the dications $[Ni(en)_2(DMF)_2]^{2+}$, $[Ni(en)_2(DMF)]^{2+}$, and $[Ni(en)_2]^{2+}$. In addition, a signal corresponding to the fragment ion $[Ni(en)(en\text{-}H)]^+$ is observed which is assigned to charge reduction in analogy to reaction 3. Similar fragmentation patterns evolve for the mixed dications with n = 1–3 (data not shown).

$$[Ni(en)_2(DMF)_n]^{2+} \rightarrow [Ni(en)_2(DMF)_{n-x}]^{2+} + x\,DMF \tag{14}$$

From the CID spectra of the dications $[Ni(en)_2(DMF)_n]^{2+}$ with n = 1 and 2, it emerges that the loss of DMF (reaction 14) is always favored, as already noted for the $[Ni(en)_3(DMF)_n]^{2+}$ cations. In addition, evaporation of neutral ethylenediamine to afford $[Ni(en)(DMF)_n]^{2+}$ (n = 1, 2) takes place at high collision energies. However, this channel is quite weak in abundance, again indicating the higher tendency of Ni(II) to bind ethylenediamine compared to DMF.

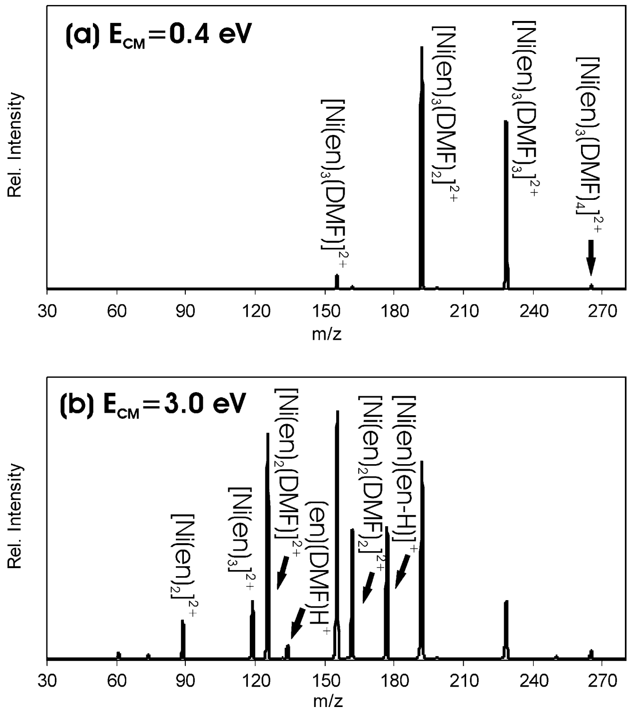

Fig. 5. CID spectra of mass-selected $[Ni(en)_3(DMF)_4]^{2+}$ ($m/z = 265$) at variable collision energies (E_{CM}).

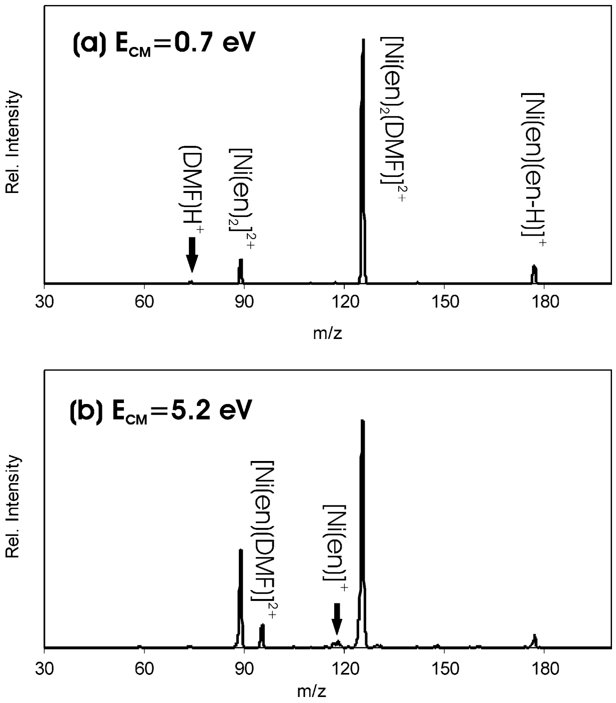

Fig. 6. CID spectra of mass-selected $[Ni(en)_2(DMF)]^{2+}$ ($m/z = 125.5$) at variable collision energies (E_{CM}).

At the stage of $[Ni(en)_2(DMF)]^{2+}$, proton transfer from ethylenediamine to DMF (reaction 15) does take place leading to the fragment ions $[Ni(en)(en\text{-}H)]^+$ and $(DMF)H^+$.

$$[Ni(en)_2(DMF)]^{2+} \rightarrow [Ni(en)(en\text{-}H)]^+ + (DMF)H^+ \quad (15)$$

Traces of the deprotonated ion $[Ni(en\text{-}H)(DMF)]^+$ formed by proton transfer between ethylenediamine molecules were also observed upon CID. Labeling experiments confirm that the hydrogen atom involved in the proton transfer according to reaction 15 stems from the amino groups of ethylenediamine.

Selected CID spectra of $[Ni(en)_2(DMF)]^{2+}$ are given in Fig. 6. At low collision energy ($E_{CM} = 0.7$ eV, Fig. 6a), simple DMF elimination leads to $[Ni(en)_2]^{2+}$ ($m/z = 89$) as well as proton transfer from ethylenediamine to DMF followed by charge separation to afford $[Ni(en)(en\text{-}H)]^+$ ($m/z = 177$) and $(DMF)H^+$ ($m/z = 74$). Further, we note that the two monocations are formed in a ratio of $m/z = 177$ and 74 of approximately 6 to 1, whereas, reaction 15 implies these monocations to be produced in equal quantities. However, this intensity difference reflects the significant instrumental discrimination of the lighter fragment in dication dissociation [57,58]. At increased collision energy ($E_{CM} = 5.2$ eV, Fig. 6b), loss of ethylenediamine does take place leading to yield $[Ni(en)(DMF)]^{2+}$ ($m/z = 95.5$). In recursion to the above discussion about the absence of the $[Ni(en)]^{2+}$ dication upon CID of $[Ni(en)_2]^{2+}$, it is interesting to note that already a single DMF ligand is sufficient for the generation of a doubly charged ion.

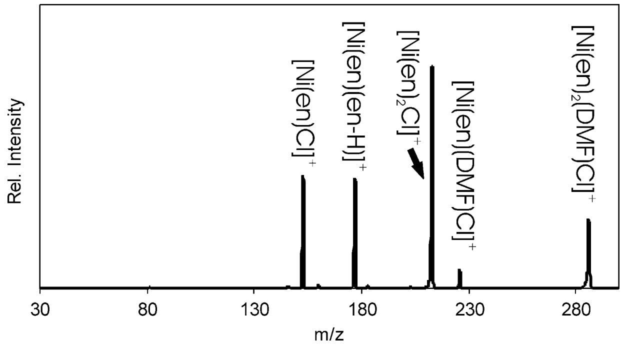

Fig. 7. CID spectrum of mass-selected $[Ni(en)_2(DMF)Cl]^+$ ($m/z = 286$) at $E_{CM} = 4.7$ eV.

The CID spectra of mass-selected $[Ni(en)_2(DMF)Cl]^+$ ($m/z = 286$) reveal preferential elimination of neutral DMF. At increased collision energy, elimination of ethylenediamine occurs to a very low extent, once more confirming the high affinity of Ni(II) for ethylenediamine. A representative CID spectrum of mass-selected $[Ni(en)_2(DMF)Cl]^+$ at $E_{CM} = 4.7$ eV is given in Fig. 7 with the loss of neutral DMF leading to $[Ni(en)_2Cl]^+$ as the major dissociation channel.

4. Conclusions

Electrospray ionization allows the generation of various Ni(II) complexes in the gas phase with ethylenediamine and

DMF as ligands. Thus, ESI of solutions of $NiCl_2$ containing ethylenediamine yields doubly charged solvated ions of the general formula $[Ni(en)_n]^{2+}$ with $n = 2$–5, singly charged ions of the general formula $[Ni(en)_nCl]^+$ with $n = 1$–3, and the chloro-bridged binuclear clusters $[Ni_2(en)_nCl_3]^+$ with $n = 2$–4. In the dicationic complexes with a large number of n, ethylenediamine appears to form a second solvation shell with the outer ligands being coordinated via hydrogen bonds.

The CID spectra of mass-selected ions reveal several modes of dissociation. The dications $[Ni(en)_n]^{2+}$ (with $n = 3$–5) show elimination of neutral ethylenediamine followed by interligand proton transfer and charge separation as the dominant processes. In contrast, the dication $[Ni(en)_2]^{2+}$ undergoes intracomplex electron transfer yielding the reduced complex $[Ni(en)]^+$ concomitant with the formation of en^+. CID of the monocations $[Ni(en)_nCl]^+$ with $n = 2$ and 3 results in ligand evaporation and competitive elimination of HCl. CID of $[Ni(en)Cl]^+$ displays eliminations of HCl and ammonia at low collision energies and expulsion of atomic $Cl^\bullet$ at elevated collision energies. CID of $[Ni_2(en)_nCl_3]^+$ results in ligand detachment followed by loss of $NiCl_2$ to yield the mononuclear complex $[Ni(en)_2Cl]^+$. Analysis of labeled ethylenediamine shows *N*-deprotonation in all cases.

In addition, some mixed-ligand Ni(II) complexes of compositions $[Ni(en)_3(DMF)_n]^{2+}$ with $n = 0$–4, $[Ni(en)_2(DMF)_n]^{2+}$ with $n = 0$–2 and $[Ni(en)_2(DMF)Cl]^+$ have been generated from solutions of $NiCl_2$ which contain both ethylenediamine and DMF. Clusters which contain exclusively ethylenediamine $[Ni_2(en)_nCl_3]^+$ ($n = 2$–4) were also generated in the presence of DMF, indicating the preferential solvation of Ni(II) by ethylenediamine. From the CID of the mixed-ligand Ni(II) complexes it emerges that evaporations of the DMF ligands are always favored, which is attributed to the chelate effect of ethylenediamine.

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