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Direct Observation of Triple Ions in Aqueous Solutions of Nickel(II) Sulfate: A Molecular Link Between the Gas Phase and Bulk Behavior

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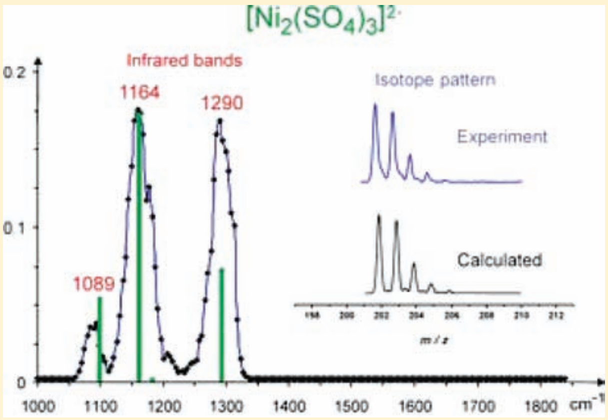
S *Supporting Information*

ABSTRACT: Electrospray ionization of an aqueous solution of nickel(II) sulfate provides direct experimental evidence for the formation of triple ions of the type $[Ni_2(SO_4)(H_2O)_n]^{2+}$ and $[Ni(SO_4)_2]^{2-}$, whose existence in aqueous solution has previously been proposed based on relaxation spectroscopy [Chen et al. *J. Sol. Chem.* **2005**, *34*, 1045]. Formally, these triple ions are formed by aggregation of the solvated ions Ni^{2+} and SO_4^{2-}, respectively, with the neutral ion pair $NiSO_4$. In addition, also higher adducts are observed, e.g. the "pentuple ions" $[Ni_3(SO_4)_2(H_2O)_n]^{2+}$ (n = 7−9) and $[Ni_2(SO_4)_3]^{2-}$, of which the dicationic is extensively hydrated, whereas the anionic is not. The structures of the dinuclear nickel clusters are derived from ab initio calculations and their infrared spectra are compared with experimental data obtained for the gaseous ions $[Ni_2SO_4(H_2O)_5]^{2+}$ and $[Ni_2(SO_4)_3]^{2-}$, respectively. The calculations show that the structures are crucially controlled by the degree of solvation of nickel ion. Explicit consideration of solvating water molecules within the first coordination sphere suggest that the dicationic triple ion $[Ni_2SO_4]_{aq}^{2+}$ is bent and thus bears a permanent dipole moment, whereas the $[Ni(SO_4)_2]_{aq}^{2-}$ dianion tends to be quasi-linear. The experimental and theoretical data for the gaseous ions thus support the elegant, but indirect, deductions previously made based on solution-phase studies.



INTRODUCTION

The detailed molecular structure of solutions of metal ions in aqueous and organic media forms a topic of intense research, both with respect to the bulk solutions as well as the air/liquid interface region.[1,2] A particular concern is the competition between complete heterolysis of a metal salt MX_z (X = monovalent counterion) into the separated solvated ions M_{solv}^{z+} and z equivalents of X_{solv}^{-} versus the formation of ion pairs, e.g. $MX_{(z-y)solv}^{y+} + yX_{solv}^{-}$. Due to the highly dynamical behavior of liquid solutions, detailed experimental information about the molecular structure of salt solutions is difficult to achieve, however. In some cases, traditional condensed-phase methods and modern spectroscopic techniques even give contradicting results.[3] Recently, Hefter discussed several examples "when spectroscopy fails",[4] among which a particularly conflicting case occurs for aqueous solutions of nickel(II) sulfate and nickel(II) perchlorate, respectively. Thus, conventional solution-phase techniques clearly demonstrate the occurrence of a significant amount of ion pairing, even in dilute aqueous solutions of nickel(II) sulfate,[5,6] whereas the corresponding perchlorate prefers dissociation.[4,7] However, UV spectroscopy does not provide any evidence for ion association in aqueous solutions of nickel(II) sulfate.[4,8] This failure of the spectroscopic methods has been assigned to the insufficient differences between the free (solvated) ions and the corresponding ion aggregates in their spectroscopic signatures as well as rapid exchange processes leading to averaged signals. By means of relaxation spectroscopy, Chen et al. could indirectly deduce the existence of the triple ion $[Ni_2SO_4]_{aq}^{2+}$, for which

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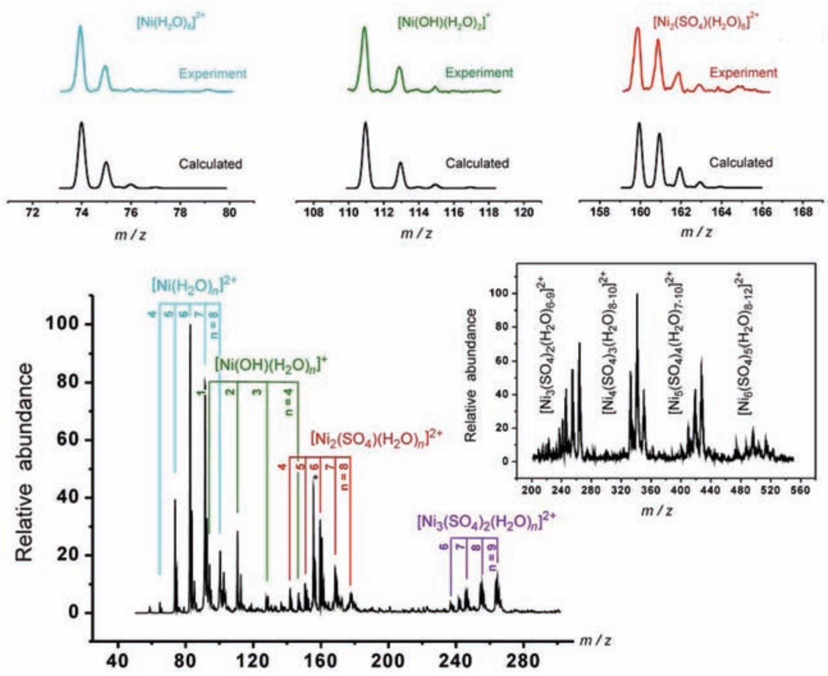


Figure 1. ESI mass spectrum of an aqueous solution of nickel(II) sulfate (c_{feed} = 10^{-3} mol/L) showing four series of microhydrated ions: the mononuclear ions $[Ni(H_2O)_n]^{2+}$ ($n = 4-8$) and $[Ni(OH)(H_2O)_n]^+$ ($n = 1-4$), the dinuclear dication $[Ni_2SO_4(H_2O)_n]^{2+}$ ($n = 5-8$), and the higher clusters $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ ($m = 3-6, n = 6-12$). On the basis of the isotope pattern, the peak at m/z 156 (labeled with an asterisk) is attributed to $[Ni(H_2O)_6(DMF)_2]^{2+}$ formed from residual *N,N*-dimethylformamide (DMF) present in the inlet system as an impurity from earlier measurements. The smaller insets on top show the experimental and the expected isotope signals for various species. The lower inset shows the higher clusters on an extended mass scale.

conceptual structural considerations suggest a bent structure and hence a permanent dipole moment; the latter is a key requirement for the detection via relaxation spectroscopy methods.[5,9] Inspired by recent results about correlations between gas-phase results obtained using electrospray ionization (ESI) mass spectrometry and solution-phase data,[10,11] we considered this particular system as a suitable test case to probe triple-ion formation using mass spectrometric techniques combined with quantum chemical methods.[12]

EXPERIMENTAL AND THEORETICAL METHODS

The mass spectrometric measurements were performed with a Finnigan LCQ Classic ion-trap mass spectrometer (IT-MS)[13] by ESI of dilute aqueous solutions of nickel(II) sulfate and nickel(II) perchlorate, respectively. In brief, the LCQ bears a conventional ESI source consisting of the spray unit (typical flow rates between 5 and 30 μL/min, typical spray voltage 5 kV) with nitrogen as a sheath gas, followed by a heated transfer capillary (kept at 200 °C), a first set of lenses which determines the soft- or hardness of ionization by variation of the degree of collisional activation in the medium pressure regime,[14,15] two transfer octopoles, and a Paul ion-trap with ca. 10^{-3} mbar helium for ion storage and manipulation, including a variety of MS^n experiments.[16] For detection, the ions are ejected from the trap to an electron multiplier. The observed isotope patterns confirm all ion assignments made in the following, although isobaric overlaps between mono- and dicationic species occur in a few cases. The expected isotopic pattern of various nickel clusters were calculated with the Xcalibur 2.0.7 software (Thermo Electron Corporation) and compared with the experimentally measured peak heights. In addition, we note that the solvated $[Ni(H_2O)_n]^{2+}$ dications reported below experience a discrimination in trapping and detection due to their relatively low mass-to-charge ratio ($m/z = 29 + 9n$ for the leading ^{58}Ni isotope).[17] Low-energy collision-induced dissociation (CID) was performed by application of an excitation ac voltage to the end-caps of the trap to induce collisions of the isolated ions with the helium buffer gas for a period of 20 ms.[18] Further, the ESI process generally is much less efficient for $NiSO_{4,aq}$ in comparison to $Ni(ClO_4)_{2,aq}$ and similar salt solutions (e.g., $Ni(NO_3)_{2,aq}$),[19] and nickel(II) sulfate requires particularly large nitrogen and sample flows in the source for a stable electrospray signal. We note that some minor interferences by complexes with residual acetonitrile as well as dimethylformamide from previous measurements were observed which coordinate rather easily to nickel.[20] For example, the peak at m/z 156 in Figure 1 (labeled with an asterisk) can be attributed to $[Ni(H_2O)_6(DMF)_2]^{2+}$ based on the isotopic pattern. While these impurities do not effect the central conclusions, in conjunction with the unusual spray conditions and the mass discrimination (see above), they lead us to refrain from a more detailed quantitative analysis of the ion abundances. In order to confirm the assignments made, the masses of the triple and pentuple ions were further determined on a SYNAPT G2 mass spectrometer (WATERS, Manchester, UK) which has as standard mass resolution of $m/\Delta m \approx$ 20000 (see the Supporting Information).

In addition, gas-phase infrared spectra of the mass-selected cluster ions $[Ni_2SO_4(H_2O)_5]^{2+}$ and $[Ni_2(SO_4)_3]^{2-}$ were recorded with a Bruker Esquire 3000 IT-MS[21−23] mounted to a beamline of the free electron laser at CLIO (Centre Laser Infrarouge Orsay, France). The ions of interest were generated by ESI from aqueous solution as described above and transferred into the ion trap. After mass selection, infrared multiphoton dissociation (IRMPD) was induced by admittance of four pulses of IR-laser light to the ion trap, resulting in a total cycling time of about half a second. For each wavelength, 8 scans were averaged to one mass spectrum which was stored, the procedure was repeated 3 times before the wavelength was changed and the data again averaged, such that each data point in the IRMPD spectra consist of 32 scans. Further, all IRMPD spectra were recorded at least two times independently, and the spectra shown are the averaged scans. In the 45 MeV range in which CLIO was operated in these experiments, the IR light covers a spectral range from about 1000 to 1800 cm^{-1}. Note that, in this kind of action spectra, the assumption that the amount of ion fragmentation is proportional to the IR absorbance is not always justified due to the multiphotonic nature of IRMPD, and the major weight is therefore put on the peak positions, rather than the peak heights in the IRMPD spectra.[24]

Ab initio calculations were performed with density functional theory using the B3LYP functional.[25] For nickel, the effective core potential Stuttgart RLC was employed,[26] and the other atoms were described by 6-31+G* basis sets as implemented in the Gaussian 03 suite.[27] For all optimized structures, frequency analysis at the same level of theory was performed in order to assign them as genuine minima or transition structures on the potential-energy surface (PES) as well as to calculate zero-point vibrational energies (ZPVEs). The relative energies (E_{rel}) of the structures given below thus refer to energies at 0 K in the gaseous state; solvation, aggregation, etc., are deliberately not included, in order to match the present experimental conditions. The stability of the wave functions was checked for all optimized structures. We note that for the $[Ni(SO_4)_2]^{2-}$ molecule in triplet spin multiplicity, we were unable to avoid one imaginary frequency in the optimized geometry, which we consider as spurious, however, because it is absent when the HF and MP2 approaches are employed. For comparison of the calculated IR spectra with the IRMPD data, we calculated the frequencies at the MP2 level with the same basis set and adopted a scaling factor of $f(\nu_{SO}) = 1.0325$ as recommended by Givan et al.,[28] whereas for all other modes, the common scaling factor of 0.98 was used.[29]

■ RESULTS AND DISCUSSION

Electrospray Ionization Mass Spectrometry. Electrospray ionization of a 10^{-3} molar aqueous solution of nickel(II) sulfate gives rise to two series of mononuclear species, i.e. the dications $[Ni(H_2O)_n]^{2+}$ and $[Ni(OH)(H_2O)_n]^{+}$ monocations, where the latter are formed via rebound of the dications with a hydroxide ion stemming from autoheterolysis of water; rebound with the monoanion HSO_4^- is negligible at this concentration. These microhydrated cations have been described repeatedly[30] and are thus not pursued any further.[31,32] In addition to the mononuclear ions, rather intense signals due to the doubly charged, dinuclear clusters $[Ni_2(SO_4)(H_2O)_n]^{2+}$ are observed upon ESI (Figure 1).[33] Furthermore, also patterns of higher clusters are discernible which can be assigned to the general composition $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ with m and n ranging up to 6 and 12, respectively.[34] These results can be regarded as a direct experimental verification of the existence of such ion aggregates in aqueous solutions of nickel(II) sulfate, specifically of the triple ion $[Ni_2(SO_4)(H_2O)_n]^{2+}$ suggested by Chen et al.[5] on the basis of relaxation spectroscopy data.

Prior to a more detailed discussion, it is important to clarify the relationship between the clusters ions seen in ESI-MS and the situation in solution. Specifically, Figure 1 shows $[Ni_2(SO_4)(H_2O)_n]^{2+}$ clusters already for feed solutions with 0.001 M, whereas the in the condensed phase notable amounts of $[Ni_2(SO_4)]_{aq}^{2+}$ clusters were only deduced above 0.5 M.[5] In fact, it is quite obvious that the concentration of the solution which is admitted to the ESI source (c_{feed}) is likely to differ from the effective concentration of the droplets in the moment of ion evaporation (c_{spray}). For the specific case of an inorganic salt dissolved in water, c_{spray} is likely to be significantly larger than c_{feed} because the solvent evaporates, whereas the salt is nonvolatile and remains in the shrinking droplets. To account for this effect, we have recently proposed a simple empirical conversion scheme $c_{spray} = f_{spray}\, c_{feed}$, where the conversion factor f_{spray} varies with c_{feed} from moderate values of about 10 for 0.01 M solutions up to 10^6 for $c_{feed} = 10^{-8}$ M.[11d,35] This purely phenomenological approach is used to approximate the gas-phase observations with a quasi-equilibrium behavior of the simple metal salts involved,[10,36] whose ionic components can be considered as being "kinetically labile" with regard to the concentration changes in the ESI process.[37,38] With respect to the data in Figure 1, the corresponding factor amounts to $f_{spray}(0.001\text{ M}) = 80$, leading to an effective concentration $c_{spray} = 0.08$ M, which at least reaches the order of magnitude of the observation of triple ions by Chen et al.[5] In this respect, we further recall the unusually large flow of drying gas required to achieve a stable electrospray of $NiSO_{4,aq}$ (see the Experimental and Theoretical Methods section), which suggests that f_{spray} most likely even is larger in this particular case. At least qualitatively, the ESI spectra are thus not in contradiction to the much more accurate data available for the bulk solutions[5,6] (also see the Supporting Information).

For comparison of the different ions observed in Figure 1, it is instructive to consider the average hydration number n_{av}. For a hydrated cation $M(H_2O)_n^{z+}$, this formal parameter is calculated as $n_{av} = \sum(n_i I(n_i))/\sum I(n_i)$, where $I(n)$ stands for the abundance of the core ion M^{z+} having n water ligands.[11c,19,39] The absolute values of n_{av} very much depend on the ionization conditions chosen, i.e. the flows of the sample and the nitrogen gas in the ESI source, the potentials applied in the interface region between the ESI source (1 bar) and the mass spectrometer (10^{-5} mbar), and the temperature of the transfer capillary which separates the region with atmospheric pressure from the first stage of differential pumping.[14,15,40] Under soft conditions, that is low temperatures and low potentials in ion transfer, multiply hydrated species prevail. With increasing temperature and/or voltages, successive evaporation of solvent molecules takes place concomitant with a continuous decrease of n_{av}. Multiple energetic collisions with nitrogen gas at further elevated potentials lead to the complete stripping of all solvent molecules ($n_{av} = 0$) and even subsequent fragmentations up to atomization.[41] Here, we have chosen reasonably soft, but not very soft conditions, which provide a good compromise between ion intensity, stability of the source, and microhydration.[42] Despite this variability, at a given setting of the ionization parameters, the relative values provide insight about the water binding energies of the ions under study.[43] In this respect, the trends observed for the cations formed upon ESI of $NiSO_{4,aq}$ are quite conclusive (Figure 1). Whereas $n_{av} = 2.7$ is found for the monocations $[Ni(OH)(H_2O)_n]^{+}$ under the experimental conditions applied, the dicationic species $[Ni(H_2O)_n]^{2+}$ and $[Ni_2SO_4(H_2O)_n]^{2+}$ both show much larger values of $n_{av} = 6.3$ and $n_{av} = 6.0$, respectively, the trinuclear dication $[Ni_3(SO_4)_2(H_2O)_n]^{2+}$ even has $n_{av} = 8.0$, and a further increase of n_{av} is apparent for the higher $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ cluster dications with $m = 4-6$ (i.e., 8.9, 9.2, and ca. 9.8, respectively; see lower inset in Figure 1). The larger values of n_{av} for the dications compared to the $[Ni(OH)(H_2O)_n]^{+}$ monocations can be simply ascribed to the increased ion−dipole interaction for the doubly charged ions. However, charge obviously does not matter alone in that n_{av} also increases with cluster size, suggesting that all nickel atoms within the larger $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ clusters are hydrated to some extent.

Clustering is also manifested in the ESI mass spectra of aqueous nickel(II) sulfate taken in the negative-ion mode in that reasonable signals for the triple ion $[Ni(SO_4)_2]^{2-}$, a small gaseous dianion,[44] the dinuclear counterpart $[Ni_2(SO_4)_3]^{2-}$ along

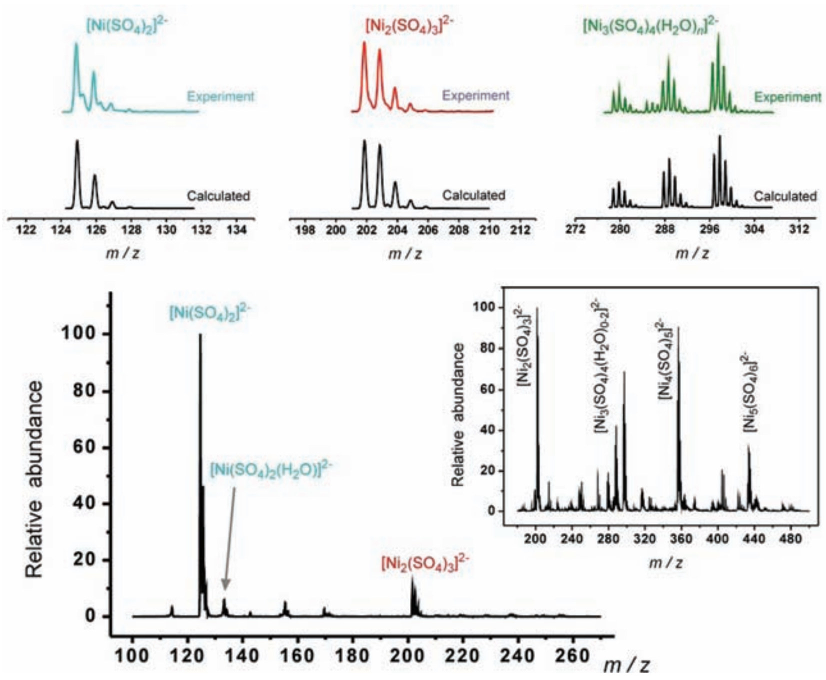


Figure 2. Negative-mode ESI mass spectrum of an aqueous solution of nickel(II) sulfate ($c_{\mathrm{feed}} = 5 \times 10^{-4}$ mol/L) showing the triple ion $[\mathrm{Ni(SO_4)_2}]^{2-}$ and the nickel cluster $[\mathrm{Ni_2(SO_4)_3}]^{2-}$. The smaller insets on top show the experimental and the expected isotope signals for various species. The central inset shows an enlarged view of the higher-mass ions $[\mathrm{Ni_3(SO_4)_2(H_2O)}_n]^{2-}$ (n = 0−2), $[\mathrm{Ni_4(SO_4)_5}]^{2-}$, and $[\mathrm{Ni_5(SO_4)_6}]^{2-}$.

with some larger clusters are observed (Figure 2). As these spectra were recorded under similar source conditions as those for the cations, it is interesting to note that most anions are not microhydrated at all and, if water ligands are attached to the clusters, their number is much lower than for the cationic systems. These observations indicate that the anionic species are less prone to hydration that the cations.[45] In this respect, the trinuclear cluster $[\mathrm{Ni_3(SO_4)_4(H_2O)}_n]^{2-}$ seems to be a notable exception because in addition to the bare ion (n = 0), also the microhydrated species with n = 1 and 2 are observed in significant amounts (n_{av} = 1.3).

In a recent review about ion pairing, Marcus and Hefter pointed out that $\mathrm{NiSO_4}$ and $\mathrm{Ni(ClO_4)_2}$ are particularly problematic cases in the comparison of results obtained by classical solution techniques and modern spectroscopic methods.[3] Thus, aqueous $\mathrm{NiSO_4}$ solutions show a significant amount of association, whereas $\mathrm{Ni(ClO_4)_2}$ largely prefers complete dissociation;[7] the UV−vis spectra of both salt solutions are identical, however.[4] Accordingly, we include a brief survey of the ESI mass spectra of aqueous solutions of $\mathrm{Ni(ClO_4)_2}$. The major ions observed correspond to the mononuclear species $[\mathrm{Ni(ClO_4)(H_2O)}_n]^{+}$ (n_{av} = 3.0), along with some contributions from $[\mathrm{Ni(H_2O)}_n]^{2+}$ dications and the hydroxide-rebound products $[\mathrm{Ni(OH)(H_2O)}_n]^{+}$ (Figure 3). At concentrations of the feed solution above $c_{\mathrm{feed}} = 5 \times 10^{-4}$ mol/L, some amounts of the dinuclear ions $[\mathrm{Ni_2(X,Y)_3(H_2O)}_n]^{+}$ (n_{av} = 4.7), and the trinuclear clusters $[\mathrm{Ni_3(X,Y)_5(H_2O)}_n]^{+}$ (n_{av} = 3.8) with X, Y = OH and $\mathrm{ClO_4}$ are observed (see inset in Figure 3). Upon comparison with Figure 1, however, it is obvious that the tendency for ion aggregation is significantly less pronounced than in the case of $\mathrm{NiSO_4}$; this is exactly what has been derived for the aqueous solution as pointed out by Marcus and Hefter.[3,4] In quantitative terms, the integral abundance of the cluster ions amounts to about 40% in the case of $\mathrm{NiSO_4}$ (Figure 1) compared to only about 10% for the equally concentrated solution of $\mathrm{Ni(ClO_4)_2}$ (Figure 3); in this context, we point out once more that the effective concentration c_{spray} in electrospray is orders of magnitude larger than c_{feed}.[11d] With regard to the clustering, it is further interesting to note that the dinuclear and trinuclear species bear similar abundances, indicating a cooperative effect in favor of the formation of the larger cluster ion, as a proportional decrease (i.e., $I_{\mathrm{monomer}}/I_{\mathrm{dimer}} \approx I_{\mathrm{dimer}}/I_{\mathrm{trimer}}$) is expected otherwise.[11c,34]

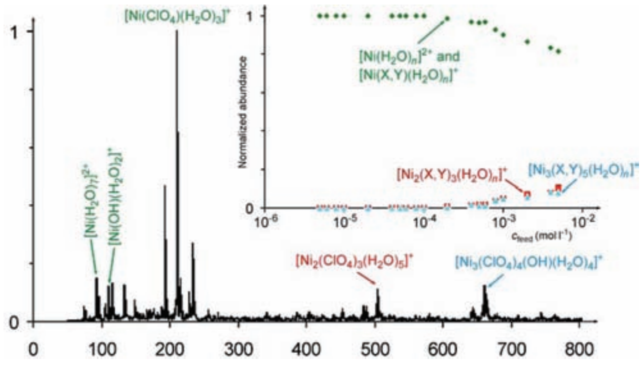


Figure 3. ESI mass spectrum of an aqueous solution of nickel(II) perchlorate ($c_{\mathrm{feed}} = 10^{-3}$ mol/L) showing the mononuclear ions $[\mathrm{Ni(OH)(H_2O)}_n]^{+}$ and $[\mathrm{Ni(ClO_4)(H_2O)}_n]^{+}$, the dinuclear clusters $[\mathrm{Ni_2(ClO_4)_3(H_2O)}_n]^{+}$, and the trinuclear species $[\mathrm{Ni_3(ClO_4)_4(OH)(H_2O)_4}]^{+}$. The inset shows the dependence of the mononuclear ions (sum of $[\mathrm{Ni(H_2O)}_n]^{2+}$, $[\mathrm{Ni(OH)(H_2O)}_n]^{+}$, and $[\mathrm{Ni(ClO_4)(H_2O)}_n]^{+}$; green diamond), dinuclear clusters (sum of $[\mathrm{Ni_2(X,Y)_3(H_2O)}_n]^{+}$ with X = OH, $\mathrm{ClO_4}$; red square), and trinuclear clusters (sum of $[\mathrm{Ni_3(X,Y)_5(H_2O)}_n]^{+}$ with X = OH, $\mathrm{ClO_4}$; blue triangle) in the ESI spectra of aqueous $\mathrm{Ni(ClO_4)_2}$ with different concentrations.

Ab initio Calculations: Structure Evolution with Degree of Solvation. As a complementary source of insight, we have performed calculations for the dinuclear clusters with various spin

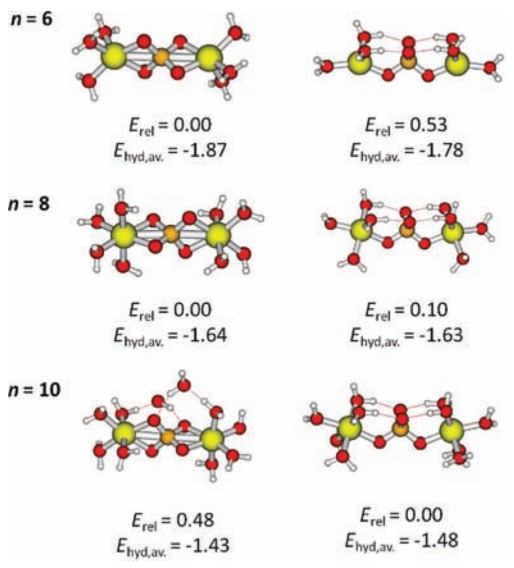
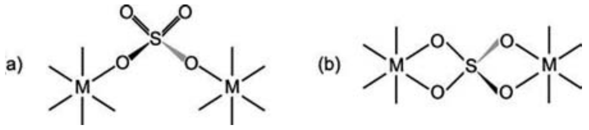


Figure 4. Optimized geometries of $[Ni_2(SO_4)(H_2O)_n]^{2+}$ in pentet multiplicity and their relative energies E_{rel} given in electronvolts. The average hydration energies $E_{hyd,av}$ are calculated as enthalpy of the reaction $[Ni_2(SO_4)]^{2+} + n\,H_2O \rightarrow [Ni_2(SO_4)(H_2O)_n]^{2+}$ divided by the number of water molecules, i.e. $\Delta E_{hyd}/n$. The coordination environment of the nickel atoms is approximately trigonal bipyramidal in the lowest energy structure for $n = 6$ and quasi-tetrahedral in the higher-energy isomer of $n = 6$. For $n = 8$, the coordination environment of the nickel atoms is quasi-octahedral in the lowest energy structure tetrahedral approximately and trigonal bipyramidal in the higher-energy structure shown. For $n = 10$, both structures are quasi-octahedral.

Scheme 1. Sketches of the Two Potential Binding Modes of a Sulfato Ligand Bridging Two Octahedrally Coordinated Metal Centers: (a) Bent Bis-monodentate Form and (b) Linear Bis-bidendate Form



multiplicities and different degrees of hydration. In all species investigated, nickel typically prefers a triplet configuration with a quasi-octahedral coordination. The corresponding species with two nickel atoms are pentets (see the Supporting Information). A key question with respect to the properties of these species in solution concerns the binding mode of the sulfato ligand. While it can safely be assumed that SO_4^{2-} acts as a bridging ligand, an important question in the present context is if it acts as a mono- or bidentate ligand for the separated metal centers. Due to the tetrahedral geometry, a bis-monodentate coordination would result in an overall bent geometry, whereas a bis-bidentate arrangement would lead to a quasi-linear structure (Scheme 1).

This difference in coordination geometry of the sulfato ligand is in fact of crucial relevance for the relaxation spectroscopic methods applied in solution, because these only detect species having a permanent dipole moment,[46] which is not the case for a linear arrangement.

If we want to address the structures of the ionic species in solution, the minimal gas-phase model must therefore have all octahedral sites of nickel saturated with either water or sulfato ligands. Let us start with $[Ni_2(SO_4)]^{2+}$, for which the minimal "aqueous" model accordingly is $[Ni_2(SO_4)(H_2O)_{10}]^{2+}$, where the sulfate ion can be either mono- or bidentate. For this "fully" hydrated ion, the monodentate structure is clearly preferred (two lower structures in Figure 4). This is, however, not true for the corresponding clusters with less water ligands, for which the structures with bidentate sulfato ligands are clearly more stable because they allow the nickel atoms to achieve a 6-fold coordination. Thus, a linear arrangement with a bis-bidendate sulfato bridge with a quasi-octahedral coordination of both nickel atoms is energetically preferred in the case of $[Ni_2(SO_4)(H_2O)_8]^{2+}$ (two central structures in Figure 4), and for the hexahydrated species $[Ni_2(SO_4)(H_2O)_6]^{2+}$ the difference is even more pronounced (two upper structures in Figure 4). Extrapolation of this behavior upon microhydration from the gas phase to the bulk solution implies that the sulfato ligands in such clusters are likely to be monodendate and thus resulting in bent structures. In contrast, the water-depleted clusters sampled in the present gas phase experiments can safely be assumed to exhibit a quasi-linear arrangement of the two nickel atoms and the sulfato ligand.

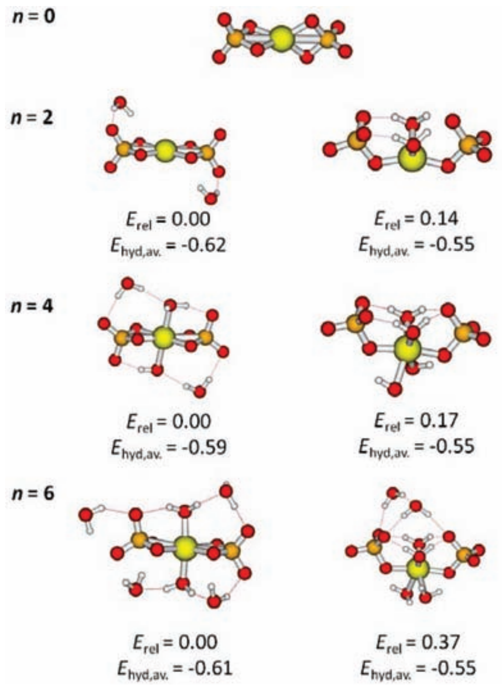


Figure 5. Optimized geometries of $[Ni(SO_4)_2(H_2O)_n]^{2-}$ isomers in triplet multiplicity and their relative energies E_{rel} given in electronvolts. Average hydration energy $E_{hyd,av}$ is calculated as reaction energy of the $[Ni(SO_4)_2]^{2-} + n\,H_2O \rightarrow [Ni(SO_4)_2(H_2O)_n]^{2-}$ process divided by the number of water molecules, i.e. $\Delta E_{hyd}/n$.

In the $[Ni(SO_4)_2(H_2O)_n]^{2-}$ anions, extensive hydrogen bonding between the water ligands and the oxygen-atoms of the sulfato ligands occurs (Figure 5). The unsolvated structure $[Ni(SO_4)_2]^{2-}$ is quasi-linear with two bidentate sulfato groups. This motif is maintained also in the solvated clusters in that hydration occurs at the outer sphere of a quasi-linear $[Ni(SO_4)_2]^{2-}$ core. The alternative monodentate structures with additional water ligands on the central nickel atoms are energetically less stable with an increasing energetic gap between monodentate and bidentate structure upon solvation.

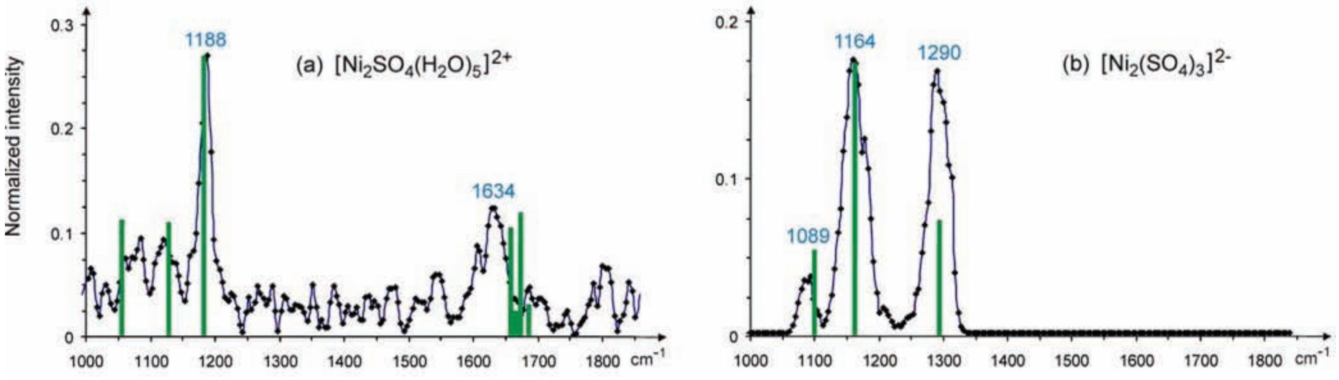


Figure 6. IRMPD spectra of (a) the mass-selected dinuclear dication $[Ni_2SO_4(H_2O)_5]^{2+}$ and (b) the mass-selected dinuclear dianion $[Ni_2(SO_4)_3]^{2-}$ in the spectral range from 1000 to 1850 cm^{-1}. The computed IR transitions are indicated as green bars. The computed structures are shown in the Supporting Information.

The computational findings fully confirm the conceptual reasoning of Hefter and colleagues, who assumed a spherical metal cation with monodendate sulfato ligands.[5,9] Thus, our computations suggest that fully hydrated $[Ni(SO_4)_2]_{aq}^{2-}$ has a quasi-linear structure and therefore is not seen in relaxation spectroscopy. In contrast, the corresponding $[Ni_2(SO_4)]_{aq}^{2+}$ species are predicted to be bent, giving rise to permanent dipole method which is hence detectable by in relaxation spectroscopy. The calculated dipole moment of the energetically most stable $[Ni_2(SO_4)(H_2O)_{10}]^{2+}$ isomer amounts to 2.0 D in the gas phase, but the dipole moment of the triple ion in solution is likely to even be larger (for a more detailed discussion see the Supporting Information). Furthermore, the calculations also provide a clue, why we mostly observe the nonsolvated dianions $[Ni_m(SO_4)_{m+1}]^{2-}$ in the negative-ion ESI measurements, whereas extensively hydrated dications $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ occur in the positive mode. Specifically, the computed average hydration energies of the $[Ni_2(SO_4)(H_2O)_n]^{2+}$ dications are about three times larger than those of the $[Ni(SO_4)_2(H_2O)_n]^{2-}$ dianions (see Figures 4 and 5) which accounts for the more extensive microhydration of the cationic species. For the anions, the reaction enthalpies of about 0.5 eV in fact reach the limit of thermal evaporation at ambient temperature.[39b]

Infrared Spectroscopy in the Gas Phase. Last but not least, two key representatives of the nickel-sulfate cluster ions were additionally characterized by infrared spectroscopy in the gas phase. To this end, the mass-selected ions $[Ni_2(SO_4)(H_2O)_5]^{2+}$ and $[Ni_2(SO_4)_3]^{2-}$ generated via ESI were stored in an ion trap and allowed to interact with infrared radiation from the tunable IR laser CLIO (Orsay, France). If the ions under study adsorb the intense IR light, fragmentation does occur which serves as the observable in this kind of spectroscopy. Because the water binding energies exceed the energy of single IR photons, sequential absorption of several photons is required and the method is accordingly referred to as infrared multiphoton-dissociation (IRMPD).[47] While the signal-to-noise ratio of the spectrum of the hydrated dication $[Ni_2(SO_4)(H_2O)_5]^{2+}$ is limited, at least two spectral features located at about 1188 and 1634 cm^{-1}, respectively, are discernible in Figure 6a. The former is assigned to the S—O stretching modes of the bridging sulfato ligands and the latter to the bending modes of the coordinated water molecules. In marked contrast, the IRMPD spectrum of the dianionic cluster $[Ni_2(SO_4)_3]^{2-}$ shows a split band for the S—O stretching modes (Figure 6b) which can be assigned to the terminal oxygen atoms (1290 cm^{-1}) and those bound to nickel (1089 and 1164 cm^{-1}), respectively; the bands at about 1600 cm^{-1} are obviously missing due to the absence of microhydration in the case of the anion.[48] For both cluster ions, the calculated vibrational frequencies (green bars in Figure 6) are in reasonable agreement with the experiments, lending support to the correct prediction of the structures using DFT. While other conformers of these ions have similar IR patterns, structures with monodentate sulfato ligands can be excluded as these are characterized by significantly blue-shifted S—O stretching modes (see the Supporting Information for a comparison).

■ CONCLUSIONS

Electrospray ionization of aqueous solutions of nickel(II) sulfate in the positive-ion mode not only generates the expected mononuclear cations $[Ni(H_2O)_n]^{2+}$ and $[Ni(OH)(H_2O)_n]^{+}$ but also the nickel clusters of the type $[Ni_m(SO_4)_{m-1}(H_2O)_n]^{2+}$ ($m = 1-6$) which formally arise from the aggregation of $[Ni(H_2O)_n]^{2+}$ with ($m - 1$) neutral $NiSO_4$ molecules. Likewise, analogous anionic $[Ni_m(SO_4)_{m+1}(H_2O)_n]^{2-}$ clusters ($m = 1-5$) are detected in the negative-ion mode, though the degree of hydration is much smaller for the anions. Our parallel ab initio calculations show that consideration of the complete coordination shell is imperative for a correct structure assignment of the investigated species. For the ions $[Ni_2(SO_4)(H_2O)_5]^{2+}$ and $[Ni_2(SO_4)_3]^{2-}$ taken as representative small clusters, reasonable agreement of the experimental infrared spectra obtained in the gas phase and the computational predictions derived from theory lends further support to the assignments made.

The observation of the gaseous ions provides direct proof for their existence also in solution as has earlier been deduced by Chen et al. based upon dielectric relaxation spectroscopy data.[5] Accordingly, this study establishes a direct molecular link between the nickel aggregates present in solution and those seen in the gas phase. In a more general sense, the present results imply that despite the dramatic changes occurring upon evaporation of the solvent in electrospray ionization of metal-salt solutions and also in the subsequent ion transfer from the ambient pressure region into a high-vacuum system, ESI mass spectrometry can serve as a useful complement of solution chemistry to identify the molecular entities present in the condensed phase.[49]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Selected high-resolution mass measurements, additional considerations about the concentration dependences and the computed dipole moments, the computed structures, and total energies, as well as the complete list of vibrational frequencies of the species shown in Figure 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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