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Infrared Spectroscopy of $Ni^+(C_2H_2)_n$ Complexes: Evidence for Intracluster Cyclization Reactions

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$Ni^+(C_2H_2)_n$ ion−molecule complexes are produced by laser vaporization in a pulsed nozzle source. These ions are mass analyzed and size-selected with a reflectron time-of-flight spectrometer. Infrared excitation with a pulsed OPO/OPA laser induces photodissociation of these complexes that proceeds by sequential loss of C_2H_2 molecules. IR resonance-enhanced photodissociation (IR-REPD) spectra are measured in the C−H stretch region for $Ni^+(C_2H_2)_n$ complexes ($n = 3-6$). The C−H stretch vibrations are shifted to lower frequencies than those in free acetylene, consistent with the formation of metal cation π-complexes. At the cluster sizes of $n = 5$ and larger, new bands are measured attributed to surface acetylene molecules. Additional red-shifted bands at $n = 5$ and beyond are assigned to an intracluster cyclization reaction, forming π-bonded cyclobutadiene.

Introduction

Transition metal π-complexes have been of longstanding interest in organometallic chemistry.[1,2] These systems have also been studied extensively in gas-phase ion chemistry,[3,4] where the reactions and energetics of size-selected complexes can be studied in detail. Metal ion π-complexes are convenient models for metal−ligand bonding and chemisorption on metal surfaces, and they have been investigated by theory.[5,6] Collision induced dissociation has been used to determine binding energies[7,8] and electronic spectroscopy has been employed to probe excited states.[9−11] Infrared and Raman spectroscopy are established techniques for organometallic complexes in the condensed phase,[12] but these methods are problematic in the gas phase. Until recently there were no IR data for transition metal ion complexes. However, our group has made recent progress in the IR photodissociation spectroscopy of transition metal ion complexes.[13−16] In this study, we report the application of this method to metal ion−acetylene complexes.

Organometallic compounds containing acetylene have been studied since Chatt and co-workers synthesized various platinum−acetylene compounds.[17−19] Using the ideas applied earlier for metal−ethylene complexes, they proposed two effects important in metal π-bonding. σ donation of π electron density from acetylene into the metal orbitals and back-donation of metal electron density into the acetylene π^* orbitals both weaken the acetylene bonding. Maitlis studied coordination complexes including nickel−acetylene by IR spectroscopy in the C≡C stretch region to investigate these issues.[20] Since then, many groups have studied metal−acetylene and −ethylene complexes to explore this so-called Dewar−Chatt−Duncanson π-bonding mechanism.[12] Another interest in organometallic chemistry, particularly for the π-complexes of nickel with acetylene, is the possibility of cyclization reactions.[2] Unfortunately, the vibrational spectroscopy of such complexes is often obscured in the condensed phase. However, gas phase measurements are solvent-free and thus in principle provide an ideal comparison to the predictions of theory. Until recently, the only vibrational spectroscopy on isolated metal π-complexes was that done in rare gas matrices.[21−25] Electronic spectroscopy on group II metal ion π-complexes was reported previously by our group[26] and by Kleiber and co-workers,[9,10] but only single-ligand complexes could be studied. Our group has recently reported the first IR spectroscopy of transition metal ion complexes using resonance-enhanced photodissociation (REPD).[13−15] $Fe^+(CO_2)_n$ and $Mg^+(CO_2)_n$ complexes were studied in the CO_2 asymmetric stretch vibration for complexes with up to 10−12 ligands. In collaboration with Meijer and co-workers,[16] we have also recently reported IR-REPD spectra of transition metal ion−benzene clusters. In the present work, we describe the application of IR-REPD spectroscopy to metal−acetylene complexes. $Ni^+(C_2H_2)_n$ species are studied in the C−H stretch region, showing how these vibrations are affected by π-bonding and providing the first evidence for cyclization chemistry in these systems.

Experimental Section

Nickel−acetylene clusters are produced by laser vaporization in a pulsed supersonic expansion. A Nd:YAG laser (355 nm) ablates a rotating nickel rod, and $Ni^+(C_2H_2)_n$ clusters are produced in an expansion of 1% acetylene seeded in argon using a General Valve. The nozzle configuration is our so-called “cutaway” source that has no growth channel downstream from the vaporization point.[27] The molecular beam apparatus for these studies has been described previously.[27] A specially designed reflectron time-of-flight mass spectrometer is employed for mass analysis of the full cluster distribution and for size selection of individual masses. Ions are pulse-extracted from the molecular beam, mass-selected by pulsed deflection plates, and photodissociated with tunable infrared light from an optical parametric oscillator/amplifier (OPO/OPA) system.[13−15] In the 2900−3400 cm^{-1} region of this experiment, the OPO produces 5−10 mJ/pulse in a 3 mm diameter spot. Fragment ions are recorded with a digital oscilloscope (LeCroy 9310) as a function of wavelength to record a spectrum.

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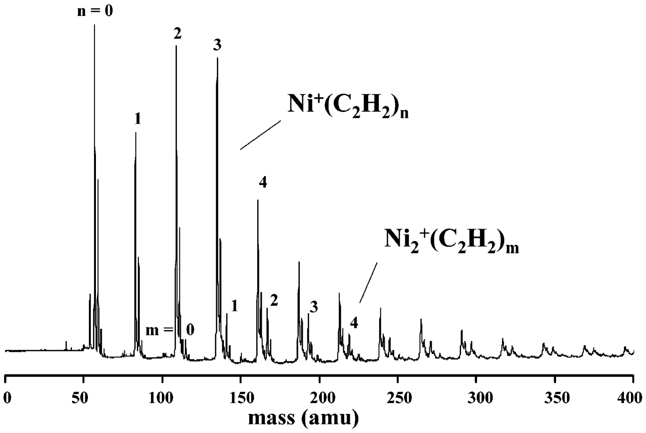


Figure 1. Mass spectrum of the $Ni^+(C_2H_2)_n$ complexes produced by the cluster source. A small amount of the $Ni_2^+(C_2H_2)_n$ complexes is also observed.

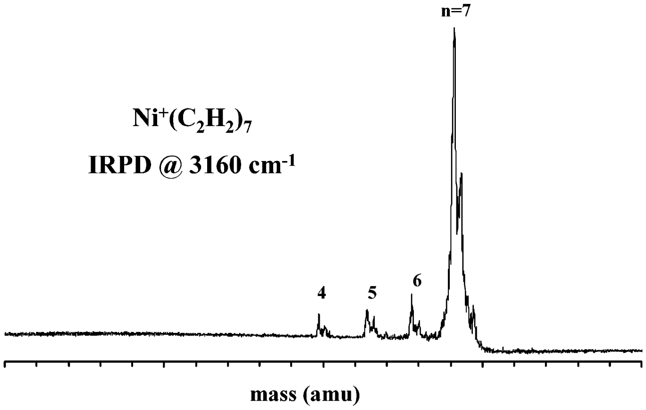


Figure 2. Photodissociation mass spectrum of $Ni^+(C_2H_2)_7$ showing the loss of one, two, or three acetylene molecules.

Results and Discussion

Figure 1 shows the mass distribution of metal ion complexes produced by the cluster source. Complexes of the form $Ni^+(C_2H_2)_n$ are produced out to beyond $n = 10$. The multiplets at each mass peak are due to the isotopes of nickel. Lower intensity peaks are also seen for diatomic nickel complexes, i.e., $Ni_2^+(C_2H_2)_m$ for $m = 1-5$. The acetylene is present primarily as whole molecules, i.e., there is little evidence for fragmentation in the laser plasma. In particular, these conditions do not produce metal carbides that are seen when early transition metals are combined in a laser plasma with acetylene.[28] However, this behavior is consistent with that seen previously for other metal ion complexes with this "cutaway" source.[27]

These clusters are size-selected and excited with IR radiation in the 2900−3400 cm^{-1} wavelength region to attempt photodissociation. No photodissociation signal is detected for the complexes $Ni^+(C_2H_2)_n$ for $n = 1, 2$. A small amount of photodissociation can be seen for the $n = 3$ complex, but dissociation is more efficient for larger clusters in the $n = 4-8$ size range. Photodissociation can also be observed for the $Ni_2^+(C_2H_2)_m$ complexes, although the signals are weak. Figure 2 shows the photodissociation of $Ni^+(C_2H_2)_7$, which eliminates up to three acetylenes. In each complex, dissociation proceeds by the loss of intact acetylene molecules. Smaller complexes lose only one acetylene, while the larger ones lose two or more.

These photodissociation trends are similar to those we have seen for other metal ion complexes.[13−15] The photodissociation yield depends on the excitation energy compared to the metal−ligand bond energy, the tendency of the complexes to absorb one or more photons, and the rate of intramolecular vibrational energy relaxation (IVR) within the complex. The dissociation energies of these complexes have not been measured, but Bauschlicher and co-workers have calculated the value for $Ni^+(C_2H_2)$ (35.1 kcal/mol; ∼12 300 cm^{-1}).[5] It is therefore clear that photodissociation of this complex near 3000 cm^{-1} requires a multiphoton process. Multiphoton dissociation is well-known in transition metal complexes when they are excited with high-intensity infrared lasers.[29,30] However, the efficiency of this process depends on the density of vibrational states needed to maintain resonance at higher vibrational levels, which is expected to be rather low in the small complexes. When a selected vibration is excited (the C−H stretch here), IVR must occur for energy to reach the weakest bond (the metal−acetylene stretch), where dissociation occurs. The IVR rate also depends on the density of states. Small clusters are therefore more difficult to photodissociate because they have higher bond energies and lower densities of states. Larger complexes should have lower dissociation energies, especially when the number of ligands exceeds the metal coordination number. Outer sphere ligands should have binding energies similar to that in the acetylene dimer ($D_0 \sim 400$ cm^{-1}).[31] It is then apparent that single photon photodissociation may occur for the larger complexes. The difficulty in dissociating small clusters and the improved yields for the larger ones are then understandable.

Both the mass spectrum and the dissociation efficiency suggest a change in cluster stability after $n = 3$. The mass spectrum has a drop in intensity here (independent of focusing conditions), and the $n \geq 4$ complexes have photodissociation yields about 10 times greater than that of the $n = 3$ complex (see below). This is consistent with a most stable coordination sphere of three acetylenes, analogous to the well-known tris(ethylene)platinum complex.[1,32] Acetylene is usually a two-electron donor, and therefore the complex $Ni^+(C_2H_2)_3$ would have 15 valence electrons. This is less than the stable 18-electron configuration often found in organometallic chemistry, but low electron counts are common in metal−acetylene complexes.

The fragmentation processes observed are wavelength dependent, as expected for resonance-enhanced photodissociation. Figure 3 shows the wavelength dependence of the $Ni^+(C_2H_2)_n$ complexes for $n = 3$ and 4. In both cases, the spectrum is measured in the $n - 1$ fragment channel. As shown, the $n = 3$ spectrum is noisy due to the difficulty in dissociating this complex, but there is evidence for broad bands near 3190 and 3260 cm^{-1}. The $n = 4$ complex has a much better signal level and three sharp bands are easily seen at 3212, 3237, and 3280 cm^{-1}. A weaker but reproducible band is seen at 3318 cm^{-1}. No IR photodissociation can be measured for the $n = 1, 2$ complexes under any conditions, as discussed above. The free acetylene molecule has symmetric and asymmetric C−H stretching vibrations at 3374 and 3289 cm^{-1}, respectively.[33] It is then apparent that the bands measured here are mostly shifted to lower frequency than the C−H stretches in acetylene itself. Such a red shift is actually expected when the metal binds to acetylene in the π configuration. According to the Dewar−Chatt−Duncanson picture of π-bonding, there is σ donation of acetylene electron density into the metal orbitals and π-back-bonding of metal electron density into the π^* orbitals on acetylene. Both factors weaken the acetylene bonding, and this results in a lowering of its vibrational frequencies. In organometallic chemistry this effect is most often measured as a red shift in the C≡C stretch vibration,[12,32,34,35] which is outside the

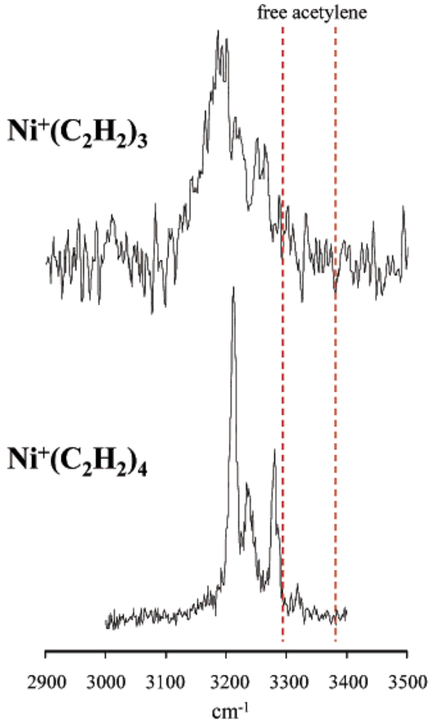


Figure 3. Resonance-enhanced photodissociation spectrum of $Ni^+(C_2H_2)_3$ and $Ni^+(C_2H_2)_4$ complexes in the infrared wavelength region near the C$-$H stretch in the free acetylene molecule. As shown, the signal level for the $n = 3$ complex is poor due to the low efficiency of photodissociation for this complex, whereas the $n = 4$ spectrum has a much better signal level.

tuning range of our OPO. However, the C$-$H modes should follow the same trend, as observed here.

Although the IR and Raman activity of the free acetylene vibrations are well-known, the IR spectroscopy here requires that we consider the symmetry of the full metal complex. For example, both the symmetric and asymmetric stretches may become IR-active in the reduced symmetry of a metal π complex. The possible IR-active vibrations in multiligand complexes include combinations of the symmetric and asymmetric C$-$H motions on different ligands. The $n = 2$ complex would have four C$-$H vibrations involving in-phase and out-of-phase combinations of the vibrations on the two ligands. In a planar structure, two IR-active modes are expected (the out-of-phase symmetric stretch and the in-phase asymmetric stretch). In the $n = 3$ complex, trigonal structures are likely. The known tris(ethylene)platinum or -palladium complexes have the three ethylene moieties in the same plane as the Pt atom in a D_{3h} structure.[12,20,32,35] If $Ni^+(C_2H_2)_3$ has this structure, then its vibrations include an in-phase combination of the symmetric stretch on all three molecules (not IR-active), a degenerate 1+2 (same as 2+1) out-of-phase combination of the three symmetric stretches (IR active), and similar in-phase (not active) and out-of-phase (active) combinations of the asymmetric stretch on all three molecules. Therefore, two IR-active vibrations are expected for this structure, and two broad bands are apparently seen. However, three IR-active bands are expected for the trigonal D_{3h} structure with the acetylenes oriented perpendicular to the plane defined by the metal and the C$\equiv$C bond centers. Considering the noisy spectrum, it is entirely possible that a third IR band with weaker intensity might be present but not detected. Without better spectra, therefore, we cannot distinguish between these structures, but the planar configuration is more likely based on known organometallic complexes. It may be possible in the future to obtain better spectra of these small clusters by enhancing their photodissociation with the rare-gas tagging method.[13−15]

The structure of the $n = 4$ complex is interesting to consider. If we add an extra ligand to the stable $n = 3$ core suggested above, then a "3+1" structure could be formed. This would likely have some of the same IR resonances seen for the $n = 3$ complex and some additional ones associated with the weaker bonded ligand. However, the strongest feature for the $n = 3$ complex at 3190 cm^{-1} is not present at all in the $n = 4$ complex. Instead, a relatively simple spectrum is observed, with its strongest band *less* red-shifted than that for the $n = 3$ complex. This implies that the $n = 4$ complex does not represent a 3+1 species. Instead, it seems that the fourth ligand has induced enough of a rearrangement to make the four ligands equivalent. However, the smaller red shift and greater dissociation yield yield for $n = 4$ indicates that the binding energy for this complex is less than that for $n = 3$. If there are four equivalent ligands, the complex would most likely have a tetrahedral structure, although a square planar species is also conceivable. A tetrahedral complex has four IR active vibrations in the region of the asymmetric stretch, analogous to corresponding IR-active modes of methane. A square planar species, if it did exist, would likely have the acetylenes oriented perpendicular to the plane containing the metal and ligand center, also with four IR-active modes. In the spectrum for the $n = 4$ complex, four bands (three strong and one weak) are evident. So the spectrum is consistent with expectations for either structure, but it does not allow us to distinguish between them. With no other evidence, we assume that the complex has the tetrahedral structure that is most common for nickel coordination complexes.[2]

Larger complexes with five, six, or more ligands are also made with good abundance, and their spectra are easily measured because their photodissociation is efficient. In these systems, both steric and electronic considerations suggest that the additional ligands at some point will not be bound to the metal. We have shown previously that the IR spectra of metal$-$$CO_2$ complexes were noticeably different for "core" ligands (attached to metal) as opposed to "surface" ligands (bound externally).[14] It is therefore interesting to investigate these effects here with acetylene.

Figure 4 shows the comparison of the spectra for the $n = 4-6$ complexes. The larger complexes have several more peaks in their spectra, but again these features fall mostly to the red of the free acetylene vibrations. Careful inspection shows that the three main bands discussed above for the $n = 4$ complex are reproduced in the spectra of the $n = 5$ and 6 complexes, albeit with small shifts. The 3212 band moves slightly to 3210 and 3208 cm^{-1} in the $n = 5$ and 6 species, with gradually diminished intensity. Corresponding to the $n = 4$ band at 3237, there are bands at 3238 and 3240 cm^{-1} for the $n = 5$, 6 complexes. The 3280 cm^{-1} band for $n = 4$ is still there for $n = 5$, but with lower intensity, and this band is barely noticeable at $n = 6$. New bands appear for the $n = 5$ complex at 3248 and 3266 cm^{-1}, and these are still present at 3248 and 3264 for $n = 6$. The 3248 band increases in intensity from $n = 5$ to 6. However, the most obvious change in the spectrum is the sudden appearance of a strong new band at 3178 cm^{-1} for the $n = 5$ complex, which is still apparent at 3176 for $n = 6$. A second new, but weaker, band emerges at 3155 for the $n = 6$ species. It is possible to assign these new bands by considering known information for pure acetylene clusters and for other metal$-$hydrocarbon complexes.

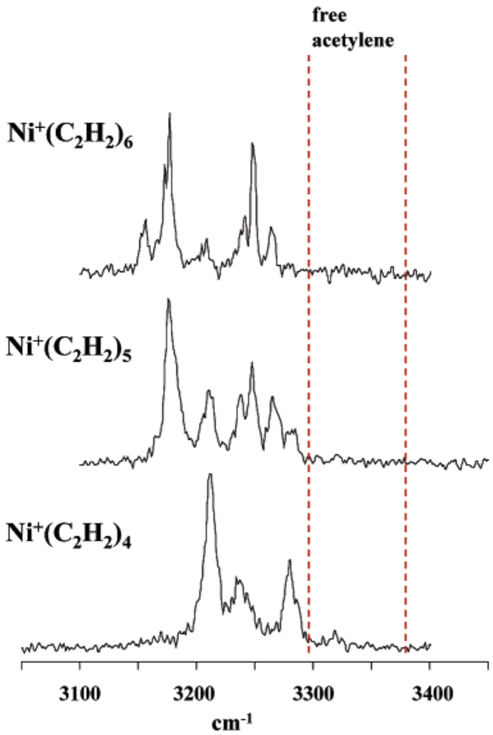


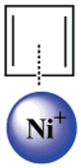
Figure 4. IR photodissociation spectra of $Ni^+(C_2H_2)_{n=4,5,6}$ complexes.

The 3248 and 3266 cm^{-1} bands can be assigned to acetylene molecules not attached directly to the metal, but instead bonded (perhaps in more than one configuration) in the second ligand layer of the cluster. This assignment is possible because the IR spectroscopy of acetylene dimer, trimer, and larger clusters has been studied previously, and these spectra fall in exactly this region.[36] It is completely reasonable that outer acetylene molecules should have IR spectra similar to those in pure acetylene clusters. Although there may be some inductive effect on the bonding by the once-removed metal ion, this should not have a large effect on the C−H stretches in the outer ligands. The red shift seen for these vibrations is relatively small even for those ligands attached directly to the metal. It is also reasonable that surface molecules would first be seen at $n = 5$ and 6. Metal−ethylene and −acetylene complexes in conventional inorganic chemistry are most stable for a coordination of three, and a slightly less stable tetrahedral coordination is perhaps also possible in the gas phase. After this, bonding directly to the metal may not provide enough energetic advantage to offset the effects of ligand crowding and the excess electron count around the metal. As additional molecules are added to the outer layer, we expect these "surface" vibrational modes to grow, and indeed our preliminary spectra of the $n = 7$ and 8 species (not shown) show that the 3248 band is still present but with even greater intensity.

In light of the assignment of peaks in the 3240−3270 cm^{-1} region to acetylene molecules in the second layer, the strong peaks at 3178/3176 for $n = 5/6$ and the weaker band at 3155 for $n = 6$ become very interesting. These bands are shifted further to the red than any others in the spectrum, but they appear only in the larger clusters. Because we have associated a red shift with the effect of a metal ion bonded in a π configuration to acetylene, why should these larger clusters exhibit a greater shift? This happens at the same cluster size when surface-bonded acetylene vibrations are first seen. Apparently, there is a new kind of perturbation arising through the "solvation effect" of second layer molecules on those in the inner coordination sphere. To cause such an additional red shift on the C−H vibrations, this interaction must be stronger than the clustering of acetylene on itself or even its π interaction with metal. The only interaction that seems to satisfy these requirements is an *intracluster reaction*. Several intracluster reactions are possible based on the known chemistry of acetylene on surfaces and in organometallic complexes.

Condensation reactions between acetylene molecules on transition metal surfaces are well-known to produce benzene,[37] and benzene has been formed from reactions of acetylene in gas-phase metal ion complexes.[38] Likewise, isomerization of acetylene on surfaces or in organometallic complexes may lead to metal−vinylidene structures.[22,37] However, the C−H vibrations of benzene lie below 3100 cm^{-1},[33] and these should shift further to the red in metal π-complexes. The metal−vinylidene C−H vibration falls near 2980 cm^{-1}.[22,37] Therefore, these species can be ruled out here. A well-known reaction of nickel with acetylene is the so-called Reppe cyclization that produces cyclooctatetraene (COT).[2] However, the C−H vibrations in COT[33] also lie near 3000 cm^{-1} and this can also be ruled out. The only other likely condensation products involve the combination of two acetylene molecules to make C_4H_4 butadiene species. Two kinds of metal−butadiene complexes are known from conventional organometallic chemistry and from surface science. The metal may be incorporated into a ring via di-σ-bonding, to form a metallacyclopentadienyl complex (I). These are known in both organometallic chemistry[1,2] and in surface science studies on transition metals[39] and silicon.[40] IR spectroscopy on organometallics of this kind are rare, but the IR studies on surfaces indicate C−H stretching vibrations in the 3030−3050 cm^{-1} region.[39,40] This corresponds well with the known vibrations for vinyl C−H in organic molecules such as propylene.[41] π-bonded η_4 metal−cyclobutadiene complexes (II) are also well-known in organometallic chemistry,[1,2,42,43] and they have even been employed in gas-phase ion chemistry.[38] Although cyclobutadiene itself is not stable, the π-bonding to the metal makes an overall stable complex. Such species were first proposed to form via a Woodward−Hoffmann allowed cyclization of two π-bonded acetylenes,[44] but in fact this route has not often been successful in practice. However, high-pressure studies have shown that direct coupling of acetylene can occur.[45] Again, IR spectroscopy studies on such metal−cyclobutadiene complexes are rare, but the existing data indicate that the C−H vibration of the cyclobutadiene attached to metal occurs near 3140 cm^{-1},[46] which is nearly the same frequency found for the isolated butadiene molecule.[33] We see bands near 3150 and 3178 cm^{-1}, which are quite close to this frequency. Therefore, the IR spectrum here agrees best with a metal−cyclobutadiene π-complex. The frequency match with previous data is not exact, but those measurements were done in solids or rare gas matrices where small frequency shifts compared to the gas phase are expected.

I. di-σ bonded $Ni^+(C_4H_4)$



II. η_4 π-bonded $Ni^+(C_4H_4)$

The intracluster formation of a metal−cyclobutadiene complex is an intriguing possibility. Although intracluster reactions in metal ion complexes have been invoked on many occasions in the past on the basis of mass spectrometry, these are the first *spectral* data to our knowledge supporting the occurrence of such chemistry. However, IR spectroscopy has been employed previously to reveal intracluster reactions in nonmetal ion clusters.[47] In the present system, the implicated chemistry does not provide any indication of a reaction in the mass spectrum. The reaction proposed is reasonable because metal−cyclobutadiene complexes for the metals iron, nickel, and cobalt all form stable complexes with cyclobutadiene in conventional organometallic chemistry.[42,43] In addition to the nickel results shown here, we have seen the same behavior for cobalt−acetylene complexes. We do not see any evidence for the elimination of a C_4H_4 group as a photofragment from any of our complexes. However, this group would be more strongly bound than π-bonded acetylene, and it would not be expected as a fragment until after all other ligands were eliminated. In our experiments, fragmentation rarely goes beyond the loss of two or three acetylene molecules. It would of course be extremely interesting to have ab initio calculations of the vibrational spectra of nickel−acetylene complexes and nickel−cyclobutadiene complexes to test these assignments. It should be noted that at the $n = 5$ cluster, we see the vibrations assigned to the "core" as well as both surface vibrations and reaction channel vibrations. Because there is not enough acetylene for these types to be present in the same complex, there must be isomers present, i.e., not all $n = 5$ complexes have reacted. At larger sizes it becomes possible to have both the reaction product and surface acetylene present in the same cluster, but isomers are then still possible.

It is interesting to note that this intracluster chemistry apparently only takes place at and beyond the cluster size of five molecules. Other examples of size-specific or so-called *cluster assisted* reactions of transition metal ions are known. For example, Bowers and co-workers have reported the onset of reactions of titanium cations with methane that begin after three molecules are present in the cluster complex.[48,49] They interpret this onset to be the result of metal ion solvation, which lowers the energy barrier to reaction on a low-lying metal excited electronic state. Nickel cations have low-lying excited states, and so such a mechanism could perhaps also explain our result. However, it may be significant that our reaction begins at the same cluster size when second-sphere ligands are seen for the first time. This could mean that acetylene molecules in the second layer (i.e., not attached to the metal) are necessary for reaction. This is understandable, because cycloaddition reactions usually require that the combining species have parallel alignment. Though the inner-sphere acetylene molecules are bound strongly in a rigid structure, the second layer molecules are bound more weakly, making it easier to achieve the configuration necessary for reaction. Consistent with this hypothesis, conventional inorganic chemistry finds that it is difficult to make cyclobutadiene directly from metal−acetylene complexes,[43] but high-pressure conditions are able to drive this kind of reaction.[45] It would be interesting to investigate earlier transition metals (chromium or iron), where greater coordination numbers are expected, to see if similar size-dependent reactions occur and to determine their onsets.

It should also be noted that *di*cyclobutadiene complexes with nickel are known in the condensed phase chemistry. In our clusters, we see the bands attributed to reaction beginning at the nominal mass of $Ni^+(C_2H_2)_5$ and these bands are present for clusters up to at least $Ni^+(C_2H_2)_8$ (the largest cluster studied). In this size range, we also see strong modes in the region assigned to the surface acetylene molecules, but the so-called core modes (i.e., the spectrum seen for the $n = 4$ complex) gradually drop in intensity. It is not inconceivable then that we have also produced such a sandwich complex in some of the larger clusters.

Conclusion

Nickel−acetylene clusters of the form $Ni^+(C_2H_2)_n$ for $n = 1-8$ are produced by laser vaporization, and their infrared spectroscopy is studied for the first time via mass-selected photodissociation experiments. Small clusters are difficult to dissociate, but the dissociation yield improves after $n = 3$. This is consistent with a most stable coordination sphere of three acetylene molecules, analogous to tris(ethylene)- or tris(acetylene)metal complexes known in conventional organometallic chemistry. The infrared excitation causes the loss of intact acetylene molecules, and the yield is enhanced on resonances in the C−H stretching region. The spectra observed fall to the red of the known C−H stretches for the free acetylene molecule, consistent with metal π-bonding. The spectrum for the $n = 3$ complex is noisy, but it indicates two bands, as expected for a planar D_{3h} structure. The spectrum for the $n = 4$ complex has three intense bands and one weak one, consistent with the number of bands expected for a tetrahedral complex. Theoretical calculations of vibrational spectra are needed to confirm these proposed structures. At the cluster size of $n = 5$ and all larger clusters studied (up to $n = 8$), new bands are observed near 3240−3270 cm^{-1}. These are assigned to external ligands by their similarity to the bands seen for pure acetylene clusters. A strong new band appears at 3175 cm^{-1} in the $n = 5$ cluster, and a second band grows in at 3155 cm^{-1} for the $n = 6$ cluster. These bands at lower frequency, which persist in all larger clusters, are assigned to an intracluster reaction product. By analogy with known organometallic chemistry, this product is concluded to be π-bonded cyclobutadiene. The intracluster cyclization reaction is suggested to begin when second sphere ligands are present so that parallel alignment between two acetylenes can be achieved.

Future studies will employ this same methodology to other metal ion−acetylene clusters, to metal ion complexes with other hydrocarbons (e.g., ethylene, butadiene, benzene), and to metal-*cluster* complexes with similar molecules. Now that size-specific infrared spectroscopy can be measured for such systems, it will be possible to investigate the details of a variety of metal−molecular reactions.

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