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Characterization of Metal–Carbon Nanocrystals in the Gas Phase: FT-ICR Studies of $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$

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Abstract: A compact supersonic source is used in conjunction with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer to generate and study the gas-phase reactivities of $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$. Sequential reactions with up to 8 H_2O molecules result in the formation of $V_{14}C_{12,13}(OH)_2(H_2O)_6^+$ and $V_{14}C_{13}(OH)_4(H_2O)_4^+$ by loss of H_2 or attachment of H_2O. Both ions are observed to attach up to 8 CH_3CN molecules. In light of an earlier study which indicated that $Nb_4C_4^+$ has a slightly distorted 2 × 2 × 2 cubic structure, these results provide evidence for the proposed 3 × 3 × 3 cubic structure of $V_{14}C_{13}^+$ where the 8 metals in the corners are the active binding sites. The similarity of the reactivity of $V_{14}C_{12}^+$ suggests an analogous structure.

1. Introduction

Since the discovery of metallo-carbohedrenes with stoichiometry M_8C_{12} (M = Ti, V, Zr, Hf, Cr, Mo, Fe),[1-7] intense theoretical investigations have focused on determining the structure of this new class of transition metal–carbon clusters. Several structures have been proposed to account for the special stability of these species.[8-18] Previously, we reported experimental results[19] consistent with the theoretically proposed low-energy T_d[10,11,17,18] or D_{2d}[12] structures, as opposed to the more symmetric T_h structure originally proposed.[1-5] Bowers and coworkers have provided evidence for a hollow cage structure for met-car clusters from elegant ion chromatography experiments.[20] Although these results suggested a T_h structure, the T_d structure could not be unambiguously ruled out. In addition to met-cars, we have recently investigated the reactivity of $Nb_4C_4^+$,[21] a 2 × 2 × 2 cubic crystallite, while Duncan's group has reported

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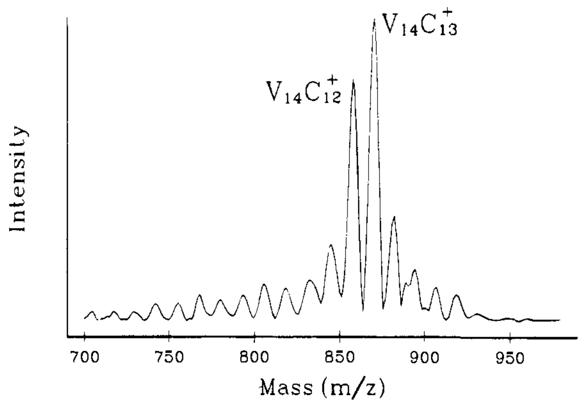

Figure 1. Mass spectrum of vanadium–carbon clusters between 700 and 950 D.

observing especially abundant peaks of higher order metal–carbon clusters exhibiting M/C ratios near 1/1, such as $M_{14}C_{13}^+$, proposed to have a 3 × 3 × 3 face-centered-cubic structure.[22,23]

The competition between the formation of the M_8C_{12} and $M_{14}C_{13}$ nanoclusters in the supersonic source has been addressed by Duncan's and Castleman's groups in terms of thermodynamic and kinetic effects.[23,24] It has been suggested that the relative concentrations of metal/carbon atoms during the condensation process influence the formation of each cluster type.[24] *Ab initio* calculations of $Ti_{14}C_{13}$ indicate that the O_h symmetry of this fcc lattice is broken down to T_d, due to the localization of the d metal electrons, and a double well with a barrier of ~13 kcal/mol is retained in its potential energy surface.[18]

In this work the vanadium–carbon clusters $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ both exhibit prominent intensities in the mass spectrum, as shown in Figure 1, permitting a comparative study of the reactivity of the two species with H_2O and CH_3CN. The results are consistent with 3 × 3 × 3 cubic structures.

2. Experimental Section

All of the experiments were performed on an Extrel FTMS-2000 dual cell Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer[25,26] combined with a compact supersonic source developed by Smalley and co-workers.[27] Laser desorption using the second harmonic of a Nd:YAG laser (532 nm) was used to generate vanadium–carbon clusters in a manner similar to Castleman and co-workers by seeding the He expansion gas with ~1% methane.[5,28] The laser power is critical to the generation of $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ under our experimental conditions. In accordance with Duncan,[22] optimum signals were obtained at low laser powers. Reagents were introduced at a static pressure (10^{-8}–10^{-6} Torr) using Varian leak valves or pulsed into the vacuum chamber using General Valve Corp. Series 9 solenoid pulsed valves.[29] Ar was used as the collision gas at a static pressure of ~3 × 10^{-5} Torr. Ion isolation[25] and collision-induced dissociation (CID)[30] were accomplished either by standard FT-ICR radio frequency pulses of variable frequency and power or by using SWIFT excitation.[31] For the rate constant measurements, Ar cooling gas was present and water and acetonitrile pressures were measured using standard procedures for calibrating the ion gauge for the sensitivity toward water and acetonitrile.[32]

3. Results and Discussion

A. Collisional Activation. Pilgrim and Duncan made the interesting observation that photodissociation of $Ti_{14}C_{13}^+$ yields sequential elimination of six Ti atoms leading to $Ti_8C_{13}^+$ which, presumably, has an endohedral metallo-carbohedrene structure with a carbon trapped inside the cage.[22] Interestingly, neither collision-induced dissociation nor multiple excitation collisional activation (MECA)[33] was able to promote fragmentation of either $V_{14}C_{12}^+$ or $V_{14}C_{13}^+$. This is in contrast to MECA on $V_8C_{12}^+$ which yielded several products.[19] One explanation is that the number of vibrational degrees of freedom is substantially higher for $V_{14}C_{12,13}^+$ than $V_8C_{12}^+$, allowing energy to dissipate more effectively. An alternate explanation is that these results imply that the binding energies of $V_{14}C_{12,13}^+$ are greater than that of $V_8C_{12}^+$. Interestingly, theoretical calculations carried out by Reddy and co-workers based on the optimized structure, i.e. fcc lattice, predict that the average binding energy is stronger for the Ti 14/13 nanocrystal (6.7 eV/atom) than for the 8/12 met-cars (6.1 eV/atom).[34]

B. Water Reactions. $V_{14}C_{13}^+$ reacts with a static pressure of H_2O at ~9 × 10^{-8} Torr and an Ar cooling gas pressure of ~3 × 10^{-5} Torr, as shown in Figure 2, by an initial addition of H_2O. Reaction with the second water proceeds by elimination of H_2 yielding, presumably, $V_{14}C_{13}(OH)_2^+$. The analogous processess have also been observed in the reactions of $Nb_4C_4^+$ and $V_8C_{12}^+$ with H_2O.[19,21] The next step is simple addition to form $V_{14}C_{13}(OH)_2(H_2O)^+$, after which two different reaction products, i.e., two reaction pathways, are observed, as proposed in Scheme 1. In pathway A, a second decomposition reaction occurs accompanied by the loss of H_2 to form $V_{14}C_{13}(OH)_4^+$, followed by four sequential additions of H_2O truncating at $V_{14}C_{13}(OH)_4(H_2O)_4^+$. In pathway B, sequential attachment of H_2O is observed to truncate at $V_{14}C_{13}(OH)_2(H_2O)_6^+$. Pathway A proceeds at a faster rate, as can be clearly seen by the intensities of the final products in Figure 2.

$M_{14}C_{13}$ (M = Ti, V, Nb) are proposed to adopt face-centered-cubic unit cell structures.[22,23] In general, a metal atom with less metal–metal coordination provides a stronger binding site. Thus, by analogy, the metal centers with the minimum metal–carbon coordination should also present better adsorption sites. The eight corner metal sites are different than the six face-centered sites and should, based on the above reasoning, bind ligands preferentially. Indeed, this is what is observed for $V_{14}C_{13}^+$ in Scheme 1, where the reactions are truncated after the attachment of eight ligands. Furthermore, Riley and co-workers have proposed that ammonia prefers to bind to the atop or apex sites of iron clusters, Fe_n^+, through an insertion of the nitrogen lone pair electrons into vacancies in the iron atom d shell.[35] Similarly, our results indicate that water prefers to occupy the atop or apex sites of vanadium atoms in $V_{14}C_{13}^+$. The failure to observe a larger coordination number may be due not only to the lower binding energy of the other sites, but also to the steric interactions between the ligands and/or to the

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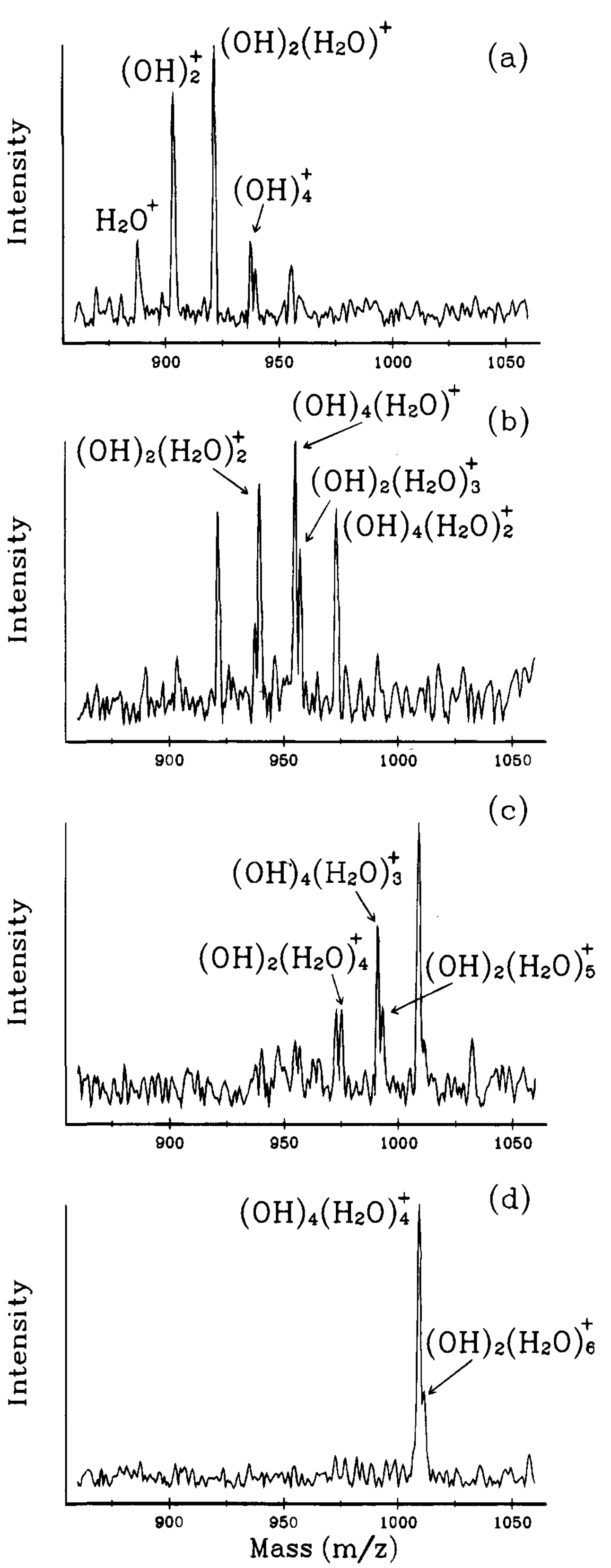
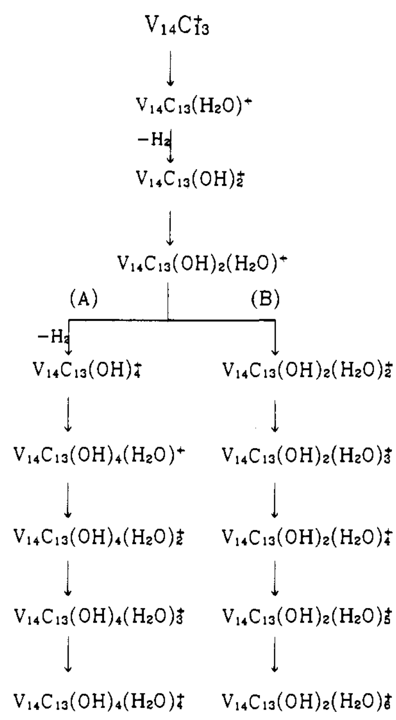


Figure 2. Reaction of $V_{14}C_{13}^+$ with H_2O ($\sim 9 \times 10^{-8}$ Torr). The reaction products correspond to $V_{14}C_{13}^+$–L, L as labeled on the spectra at various reaction times: (a) 1.5 s; (b) 2.5 s; (c) 4 s; (d) 6 s.

relatively low reagent pressures used in the FT-ICR experiment.[36] A steric effect is not likely, however, as discussed later.

Scheme 1



In analogy to the reactions of $V_{14}C_{13}^+$ with H_2O, $V_{14}C_{12}^+$ attaches the first H_2O and then undergoes H_2 elimination with the second water to generate $V_{14}C_{12}(OH)_2^+$. This is followed by the sequential attachment of 6 H_2O molecules, truncating at $V_{14}C_{12}(OH)_2(H_2O)_6^+$, as shown in Figure 3. This reaction pathway is exactly analogous to pathway B for $V_{14}C_{13}^+$ with H_2O. The reaction products and the truncation at eight attached ligands suggest $V_{14}C_{12}^+$ has the same basic cubic structure as proposed for $V_{14}C_{13}^+$. In a related study, Bowers and coworkers reported that $Ti_8C_{11}^+$ and $Ti_8C_{13}^+$ possess similar round cage structures like that of $Ti_8C_{12}^+$ metallo-carbohedrene.[20] The differences in reactivity between $V_{14}C_{12}^+$ (proceeds by pathway B) and $V_{14}C_{13}^+$ (proceeds mainly by pathway A) are likely due to differences in electronic structures, given that they have, presumably, similar geometric structures.

The water reactions involve breaking 2 H–OH bonds to form H_2. This process could originate from a concerted loss of H_2 from 2 bound H_2O molecules or oxidative addition/reductive elimination involving making and breaking the metal–H bonds during dissociative adsorption of H_2O. Riley et al. have suggested that the concerted mechanism is operative in the decomposition reaction of D_2O with bare iron clusters, where D_2 loss is observed.[37] Furthermore, dissociative chemisorption involving d orbital participation has been cited in studies of H_2, D_2, and O_2 on bare transition metal clusters.[38-41]

C. Acetonitrile Reactions. The coordinative saturation of the cluster was studied using CH_3CN to determine whether all 14 vanadium atoms are in equivalent sites. Despite its stronger dipole moment, once again a maximum uptake occurred at eight attachments, as illustrated in Figure 4. Interestingly, all of the ion intensities of $V_{14}C_{12,13}^+$ eventually shift to $V_{14}C_{12,13}(CH_3CN)_7(H_2O)^+$ and $V_{14}C_{12,13}(CH_3CN)_8^+$. This, once again, indicates that a similar structure and character can be found for both

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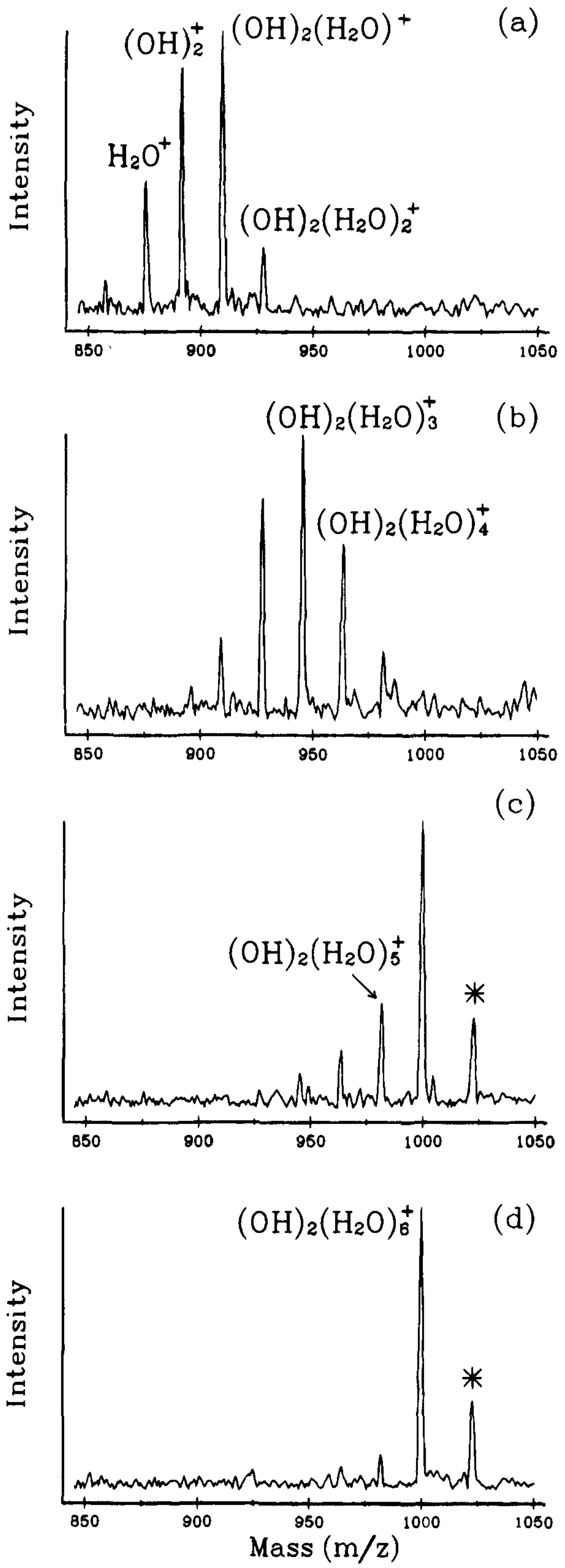

Figure 3. Reactions of $V_{14}C_{12}^+$ with H_2O (~5.9 × 10^{-8} Torr) at increasing reaction time. The reaction products correspond to $V_{14}C_{12}^+-L$, L as labeled on the mass spectra at various reaction times: (a) 2 s; (b) 4 s; (c) 6 s; (d) 7 s. The peak with an asterisk does not correspond to any combination of $(OH)_n$ and $(H_2O)_m$ attached on 14/12. However, it can be assigned as $V_{14}C_{12}(OH)_2(H_2O)_5(CH_3CN)^+$, probably due to the residual CH_3CN in the ICR cell.

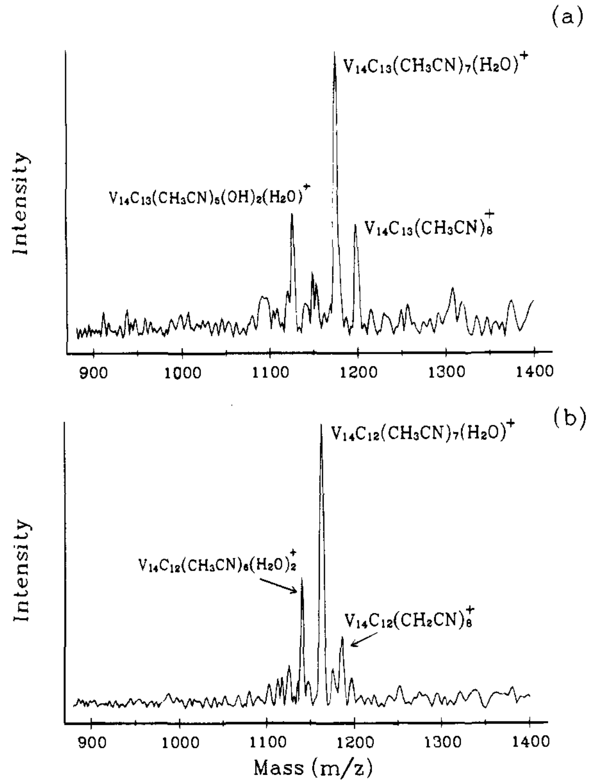

Figure 4. (a) Reactions of $V_{14}C_{13}^+$ with CH_3CN (~1.6 × 10^{-6} Torr) for 6 s. (b) Reactions of $V_{14}C_{12}^+$ with CH_3CN (~1.6 × 10^{-6} Torr) for 7 s.

species (14/12 and 14/13). However, it is surprising that $V_{14}C_{12,13}(CH_3CN)_7(H_2O)^+$ predominates over $V_{14}C_{12,13}(CH_3CN)_8^+$, since trace water in the CH_3CN reagent should only show up as a minor contribution. The observation of the less dominant $V_{14}C_{12,13}(CH_3CN)_8^+$ ion could be due to steric interactions or binding energy effects. Note that this experiment was run on several days under different circumstances.

According to the *ab initio* calculations on $Ti_{14}C_{13}$, the $Ti_{apical}-Ti_{apical}$ bond length is approximately 4 Å.[18] If $V_{14}C_{13}^+$ has a similar geometric structure, then the CH_3CN molecules should be sufficiently spatially separated without serious steric interactions occurring. The difference in binding energies could provide a reasonable explanation. It has been found that the bond strength of the bare metal clusters with ligands, i.e. NH_3, decreases linearly with the increasing number of adsorbed molecules.[42] Since the electrostatic interaction is the major component between the metal atoms of the clusters and the ligands, the behavior of the weakening of the cluster–ligand bond with increasing coverage is suggested to be due to the electron transfer of the ligands to the metal, causing the reduction of electrostatic bonding. Although the relative importance of electrostatic and dative bonds and the extent of the electron transfer in different ligands are still not clear, it appears that the H_2O with a weaker dipole moment enhances the stability of the $V_{14}C_{12,13}(CH_3CN)_7(H_2O)^+$ ion.

D. Reaction Kinetics for Water and Acetonitrile. Pseudo-first-order kinetics are observed for the reactions of $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ with H_2O and CH_3CN in the presence of Ar, indicating, but not unequivocally, that the ions are thermalized and consist predominantly of single isomeric structures. The slopes of the pseudo-first-order plots are used with the estimated pressures to obtain the observed rate constants, and the reaction efficiencies are calculated by comparing the measured rate constant, k_{ob}, to the Average Dipole Orientation rate constant,

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Table 1. Rate Constants (cm^3 molecule^{-1} s^{-1}) and Calculated Reaction Efficiencies for the Reactions of $V_{14}C_{12}^+$ with Water and Acetonitrile

reagent	k_{ob}	k_{ADO}[43]	reaction efficiency (%)
water	7.8×10^{-10}	2.1×10^{-9}	37
acetonitrile	8.1×10^{-11}	2.9×10^{-9}	2.8

Table 2. Rate Constants (cm^3 molecule^{-1} s^{-1}) and Calculated Reaction Efficiencies for the Reactions of $V_{14}C_{13}^+$ with Water and Acetonitriles

reagent	k_{ob}	k_{ADO}[43]	reaction efficiency (%)
water	1.2×10^{-9}	2.1×10^{-9}	57
acetonitrile	2.2×10^{-10}	2.9×10^{-9}	7.6

k_{ADO}, which is an estimate of collision frequency.[43] The parameters for each molecule, such as the polarizability (α), and the dipole moment (μ_D) used for calculating k_{ADO}, are given in ref 44. k_{ob}, k_{ADO}, and reaction efficiencies (k_{ob}/k_{ADO}) for $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ are summarized in Tables 1 and 2, respectively. The reactions of both ions are faster with H_2O than with CH_3CN and are found to be up to 37% and 57% efficient for the 14/12 and 14/13 ion clusters, respectively.

4. Summary

$V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ are found to react with H_2O via a combination of H_2 elimination and H_2O association reaction mechanisms. The process involving loss of H_2 occurs once and twice to form $(OH)_2$ and $(OH)_4$, respectively, for $V_{14}C_{13}^+$, while only $(OH)_2$ adducts are observed for $V_{14}C_{12}^+$. In contrast to the water reactions, the reactions of both ions with acetonitrile involve only addition reactions. All of the reactions with H_2O and CH_3CN truncate sharply at eight attached ligands. Taken in total, these results for $V_{14}C_{12}^+$ and $V_{14}C_{13}^+$ are consistent with the behavior of a cubic structure. The enhanced stability of the $(CH_3CN)_7(H_2O)$ attachment on 14/12 and 14/13 may present a good candidate for understanding the role of electron transfer in metal–ligand interactions on the clusters. Additional theoretical calculations would be helpful in understanding the role of electronic structure on the reactions of $M_{14}C_{13}$ and $M_{14}C_{12}$ species.

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