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Photoelectron Spectroscopy of V_x(Coronene)$_y$ and Ti_x(Coronene)$_y$ Anions

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Gas-phase anion complexes are produced containing one or more vanadium or titanium atoms bound to one or more molecules of the polycyclic aromatic hydrocarbon (PAH) coronene ($C_{24}H_{12}$). These species are prepared with coincident laser vaporization of a metal rod and a pressed pellet of coronene in a pulsed-nozzle cluster source. The anion complexes produced are mass-selected with a time-of-flight spectrometer and photoexcited with various Nd:YAG laser harmonics. A magnetic bottle instrument is employed for time-of-flight photoelectron spectroscopy measurements on these complexes. Electron affinities (EA's) are observed to be greater for the organometallic complexes than they are for the isolated metal clusters or the isolated coronene molecule. EA's increase with the number of metal atoms in the complex. The spectra observed for V−coronene complexes are similar in appearance to those seen previously for V−benzene and V−C_{60}, suggesting that the metal binds as a π complex in a symmetric ring site. V−(coronene)$_2$ complexes exhibit different spectra under different conditions attributed to the formation of sandwich and external-metal isomers.

Introduction

Metal π complexes with aromatic molecular ligands exhibit unusual bonding which has fascinated organometallic chemists for many years.[1] Ferrocene[2] and dibenzene chromium[3] were early examples of these systems, but this is now a rather large subfield of organometallic chemistry. The diversity of metal π complexes has increased dramatically in recent years with the development of gas-phase experiments in which metal vapor can be combined directly with unusual ligands in nontraditional synthetic schemes. There are many experimental and theoretical studies of metal benzene complexes.[4−12] Kaya and co-workers have described multimetal/multibenzene complexes that are proposed to have multidecker sandwich structures, and other ligands[13] also are found to follow this structural pattern. Exohedral metallofullerenes[14−19] and metals bound to polycyclic aromatic hydrocarbons (PAH's)[20−29] have been described recently in molecular beam experiments and in mass spectrometry. Multidecker sandwiches and other network structures have also been proposed for some of these systems. These new π complex clusters have never been isolated, but their structure and bonding properties are nonetheless interesting. Although metal−PAH complexes have attracted considerable attention, there has so far been no spectroscopy on these systems. We report here the first investigation of spectroscopy for a metal−PAH complex in the form of photoelectron measurements on vanadium and titanium anion complexes with coronene.

PAH complexes with metal are interesting for a variety of reasons. Theoretical models of metal intercalated graphite or metal binding at carbon nanotube walls often employ PAH molecules as models representing a finite section of a carbon surface, but there is virtually no experimental data for the structures or energetics of these complexes. Coronene ($C_{24}H_{12}$) is the smallest PAH having the essential structural elements of graphite. Ionized PAH's have been implicated as carriers of the optical diffuse interstellar bands (DIB's) or the unidentified infrared bands (UIR's),[30−33] and metal−PAH complexes have also been suggested to form in interstellar gas clouds.[20−22,34−38] Attachment to PAH surfaces is proposed to account for the depletion of certain metals (iron, magnesium, etc.) in the interstellar medium compared to their solar abundance. The spectroscopy and photochemistry of isolated PAH molecules are well-known,[39−43] but there is almost no information about these properties for metal−PAH complexes.

Atomic metal ion complexes with selected PAH species (including coronene) were first prepared in mass spectrometry experiments by Dunbar and co-workers.[23] In recent laboratory work, our group has described the formation and photodissociation of metal and multimetal complexes with coronene and other PAH systems.[24−29] Coronene is particularly interesting for metal experiments because it is large enough to afford multiple binding sites for metal attachment on its surface. Interior or exterior rings are available for π bonding on one or both sides of the organic surface. In the case of iron-coronene complexes, photofragmentation processes suggest that iron forms a strong covalent bond with the PAH surface, that sandwich structures are quite stable, and that in multiple-metal complexes the iron binds as separated atoms on the coronene surface.[24] Competitive binding experiments with coronene, C_{60}, and benzene were used to establish a hierarchy of binding strengths to iron.[25] In the case of chromium and other transition metals, evidence is found for the formation of clustered metal on the coronene surface, and multimetal-filled sandwiches were suggested.[27] Niobium was found to attack PAH ring systems leading to ring fracture and eventual metal carbide formation.[28] The evidence to date on metal−PAH structures come solely from photodissociation

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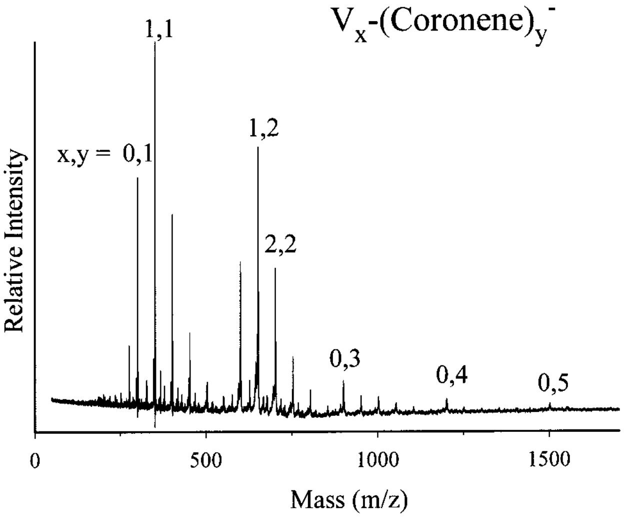

Figure 1. Mass distribution measured for V_x−(coronene)$_y$ anions produced by laser ablation/vaporization of a film-coated vanadium rod. A similar distribution is observed for titanium−coronene clusters.

patterns, as no spectroscopic data has yet been measured. We address this problem here with the first spectroscopy measurements on metal−PAH complexes.

Laser photoelectron spectroscopy of anions has been employed previously to study metal clusters and complexes that are problematic for high-resolution spectroscopy. This method has been applied to study pure metal clusters of vanadium[44−46] and titanium[47] to explore the trends in electron affinities with cluster size. Similar measurements have been performed on vanadium−benzene,[11b] vanadium−C_{60} complexes[19g] and other metal−C_{60} complexes.[19f] The application of this method here and the comparison to previous work make it possible to obtain considerable insight into the energetics and structures of metal−coronene clusters.

Experimental Section

Clusters for these experiments are produced by laser vaporization in a double-rod pulsed nozzle cluster source.[48] The samples for these experiments are a solid rod of the metal (vanadium or titanium) and a solid rod of coronene produced by high-pressure pressing of the powder into a pellet. Coincident laser vaporization of the two samples is accomplished with the focused output of two Nd:YAG lasers (second harmonic, 532 nm) in a pulsed nozzle (General Valve) source. Cluster growth occurs in a channel extending beyond the vaporization point. The negative ions produced directly by laser vaporization are sampled with a time-of-flight mass spectrometer with pulsed acceleration plate voltages.

Mass-selected photoelectron spectroscopy experiments take place in the same time-of-flight mass spectrometer, in which the arrival at the laser photodetachment region allows size selection of cluster masses. Electron time-of-flight measurements take place in a magnetic bottle spectrometer. The operation and calibration of the instrument for these experiments has been described previously.[11b,19f] Cluster anions are excited with a pulsed laser (Nd:YAG; 532 or 355 nm). Laser power and wavelength studies are employed to investigate the possibility of multiphoton processes.

Results and Discussion

Figure 1 shows the mass spectrum measured when anion clusters are grown by laser vaporization. There is no ionization process other than the growth process in the plasma generated by the vaporization laser. The anions are extracted from the molecular beam with pulsed mass spectrometer acceleration voltages. As shown, a variety of V_x(coronene)$_y$ masses are produced. All the more intense peaks observed correspond to simple multiples of vanadium and coronene. Clusters are formed which contain up to five vanadium atoms in complexes with one coronene molecule, up to four vanadium atoms in complexes with two coronene molecules, and up to four vanadium atoms in complexes with three coronene molecules. For complexes with one or two coronene molecules, the most prominent mass peaks are those with a single metal atom, and the intensities of multimetal complexes fall off gradually with size. In the lower mass region, there are essentially no pure metal clusters. This suggests that the complexes here grow primarily as metal atoms are added one-by-one to the organic surface, rather than by the combination of clustered metal with the organic. A similar anion mass distribution is obtained for titanium−coronene.

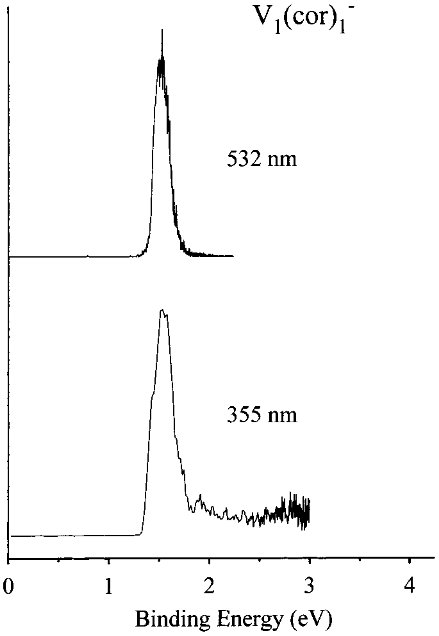

Figure 2. Photoelectron spectrum of V−coronene at 532 and 355 nm that exhibits a sharp threshold peak.

Figure 2 shows the photoelectron spectra of V−coronene at 532 and 355 nm. The spectrum consists of one strong peak with the peak intensity centered at approximately 1.5 eV. The onset of this feature provides a vertical electron affinity value of 1.38 eV. The strong sharp feature suggests that there is a vertical transition with minimal geometry change between the anion and the neutral complex. The EA value found here is significantly greater than the value for the free vanadium atom (0.525 eV) or the free coronene molecule (0.47 eV), indicating that the V−coronene anion is more strongly bound than the corresponding neutral. A similar sharp threshold peak with about the same EA value indicated is measured for Ti−coronene (data not shown).

Kaya and co-workers have previously studied the V−benzene anion using these same methods.[11b] Significantly, they find that V−benzene also has an EA (0.62 eV) greater than either V or benzene but much less than that seen here for V−coronene. The appearance of the V−benzene photoelectron spectrum is almost identical to the one shown here, with a strong sharp threshold peak. The spectrum in V−benzene was concluded to arise from detachment of a nonbonding a_1 orbital for a complex

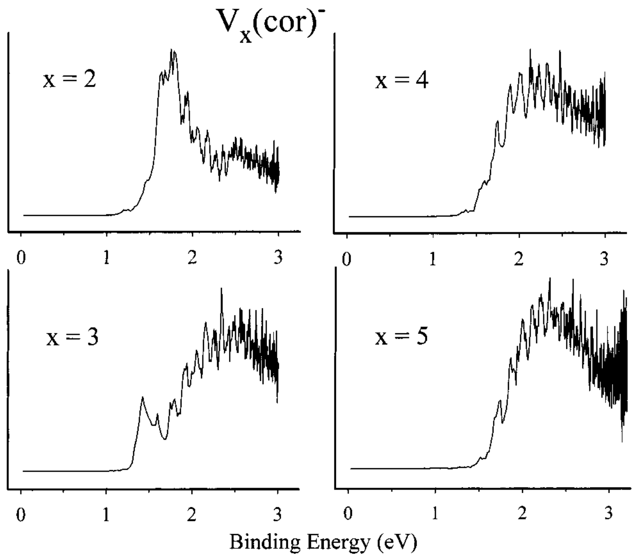

Figure 3. Photoelectron spectra of V_x−coronene clusters for $x = 2-5$ measured at 355 nm.

with D_{6v} symmetry. The similarity of the spectrum here to that one suggests that the orbital nature of the photodetachment process is similar in the two cases. Therefore, it is likely that V−coronene (and Ti−coronene) is also a π complex with the metal located in a η^6 ring site.

Although η^6 binding in a ring site on coronene is not particularly surprising, it is interesting to consider which kind of ring site might bind metal most effectively (central versus outer). Analysis of the ring currents in coronene via NMR spectroscopy and associated theory suggest that the outer ring sites possess significantly more electron density than the central ring and that there is an alternation in electron density around the six outer rings.[49] Metal π bonding is likely to be favored in regions of higher electron density, and so binding in an outer ring site is perhaps more likely than it is for the central site. This tendency has been discussed before for neutral and cation coronene complexes with other metals, and it seems likely that a similar effect would be found for vanadium. The sharp threshold peak suggests that the anion and neutral have similar structures, and so a similar "outer-ring" binding tendency is likely to apply for these anions. It is not clear where the extra charge density from anion formation will occur and how this might alter this way of thinking.

Figure 3 shows the spectra measured for V_x−coronene anions for $x = 2-4$. While the $x = 2$ spectrum has a somewhat sharp feature near the onset, the other spectra exhibit broad contours. Ti_2−coronene (not shown) has a similar, but even sharper, threshold peak, while other Ti_x−coronene spectra are also broad like those shown for vanadium. The EA values derived for each cluster size are shown in Table 1, where they are compared to the values measured previously for pure vanadium and titanium metal clusters and for coronene. As shown in the table, the corresponding metal−coronene complexes have significantly greater EA values than the metal atoms and metal dimers. V_2−coronene has the lowest EA of the M_x−coronene species studied, while Ti_2−coronene has the highest value. This latter value is interesting because the EA of Ti_2 itself has not been measured, presumably because it is so low that the anion cannot be produced effectively. In the $x = 3-5$ range, all the M_x−coronene species have EA's about the same as or slightly greater than the corresponding pure metal species.

TABLE 1: Vertical Electron Affinities (eV) for the Metal−Coronene Clusters Studied Here Compared with Pure Metal and Pure Coronene Clusters Studied Previously

species	EA (M_x)	EA (M_x−coronene)	EA (M_x−coronene$_2$)
x = 0	−	0.47[a]	0.67[a]
V	0.525	1.38(7)	0.91(14)
V_2	0.26[b], 0.522[c]	1.12(6)	1.36(31)
V_3	1.10[d], 1.01[e], 1.107[c]	1.24(19)	
V_4	1.40[d], 1.32[e]	1.40(21)	
V_5	1.26[d]	1.49(19)	
Ti	0.079	1.31(6)	1.28(6)
Ti_2	−	1.53(13)	
Ti_3	1.18[f]	1.19(15)	
Ti_4	1.21[f]	1.31(8)	
Ti_5	1.17[f]	1.36(12)	

[a] Ref 29. [b] Kaya and co-workers, unpublished. [c] Ref 47. [d] Ref 44. [e] Ref 45. [f] Ref 46.

These data show that there is a significant difference in the electronic structure of the atomic and diatomic metal−coronene complexes compared to the pure metal species. The differences are less evident in the larger cluster sizes. Larger clusters of other transition metals (e.g., chromium) on coronene exhibit photodissociation patterns in which intact M_x clusters are eliminated as a unit, indicating that the metal aggregates preferentially on the same side of the organic ring system.[27] If this also happens here, then it is understandable that the EA values in larger complexes become more like those in the pure metal clusters. The bond energies for these metals with the coronene ring are unfortunately not known. However, the bond energies in the neutral and cation vanadium clusters are known as are those in the titanium cation clusters. Except for V_2 (D_0 = 1.42 eV), the M_x−M bond energies are in the range of 2.3−3.7 eV,[50] indicating relatively strong metal−metal bonding. The bond energies for V−benzene$^+$ and Ti−benzene$^+$ are 2.42 and 2.68 eV,[8] respectively, and those for M−coronene should be comparable, or even greater.[27] Thus, it is conceivable in the small size range that metal−coronene could take precedence over metal−metal interactions, but once the coronene surface is covered (about three metal atoms should do this), then metal clustering should be more probable and EA values should be more like those for the pure metal clusters.

Figure 1 shows that in addition to the M_x−coronene clusters a variety of M_x−(coronene)$_y$ clusters are formed, where $y = 2$, 3. It is natural to consider the possibility that these species might represent sandwich structures. Indeed, such sandwiches have been suggested before in the photodissociation studies of cation metal−coronene clusters.[24−27] Figure 4 shows the photoelectron spectra measured for the V−(coronene)$_2$ complex under different conditions at both 532 and 355 nm. Inspection of these spectra shows that their onset occurs near 1.0 eV, and a vertical EA value of 0.91 (14) is assigned. However, during the course of the measurements, it became apparent that a peak near 1.5 eV was seen in some spectra but not in others. Careful investigation of the experimental conditions shows that this peak is observed at both detachment wavelengths but only under certain conditions involving the timing of the vaporization lasers on the metal and coronene samples. Under "normal" conditions (i.e., those used to take the data shown in Figures 1−3), the metal sample is located upstream in the gas flow and the coronene sample is located downstream. The separation between samples is about 1 cm. The vaporization laser for the coronene sample is fired first and that for the metal is fired 17−30 μs later (adjusted to optimize the signal). These conditions were used to obtain the spectra shown as a at both wavelengths, where the 1.5 eV peak is present. The b spectra were obtained reproducibly whenever the metal sample laser was fired about 2 μs before the coronene sample laser, and the 1.5 eV peak is missing in these.

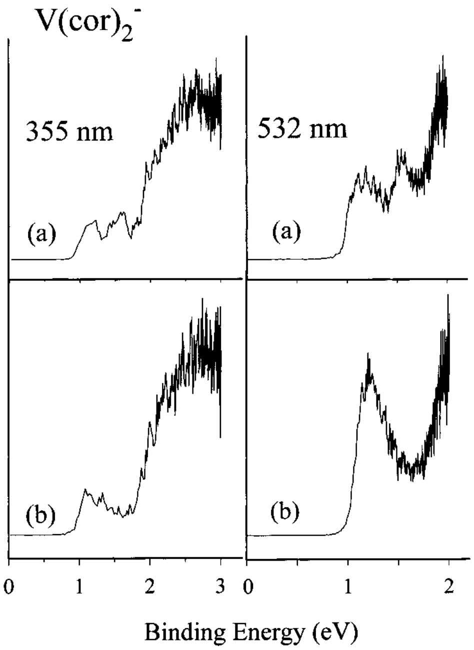

Figure 4. Photoelectron spectra of V−(coronene)$_2$ measured at 532 and 355 nm with different timing between the two vaporization lasers. The upper traces (a) show spectra obtained when the coronene sample is vaporized first, while the lower traces (b) show the spectra when the vanadium sample is vaporized first. The peak at about 1.5 eV that appears in the trace a spectra is attributed to an external-metal isomer, while the other features in trace a that also appear in the trace b spectra are attributed to the sandwich isomer.

The interpretation of these spectra is straightforward and appealing. The 1.5 eV feature must correspond to an isomeric structure produced only when the laser timing is adjusted to optimize it. It is furthermore easy to decide what kind of isomer this must be. The clusters are mass-selected, and so we know that they are composed of only one vanadium atom and two coronene molecules. The simplest isomers possible are those involving sandwich or nonsandwich structures. When the coronene is vaporized first as in spectra a, coronene molecules are present initially in the vapor without metal and pure coronene clusters can form. The substantial stability of coronene dimer has been discussed previously.[26,29] If dimers form, the growth of a sandwich isomer requires insertion of a metal atom between the coronene rings, and this is not likely to be efficient. It is more likely that at least some metal atoms will bind externally in nonsandwich configuration, e.g., a ||• configuration. When metal is vaporized first as in spectra b, coronene monomers are more likely to encounter metal before forming coronene clusters. Sandwich isomers, e.g. |•|, are then more likely to form than are external metal isomers. By this reasoning then, the 1.5 eV feature present in spectra a but not in spectra b represents an external metal isomer. It is striking that this feature occurs at 1.5 eV, which is exactly the same energy as the sharp threshold peak seen for the V−coronene complex. From the standpoint of the electronic structure near the metal, the V−coronene complex (|•)and the external V−(coronene)$_2$ complex (||•)have the same environment, and so they should have similar spectra. By deduction, then, the spectrum seen in b without the 1.5 eV peak must correspond to the sandwich isomer. It is formed predominantly under both conditions, and has a significantly lower EA than the external metal isomer.

Interestingly, Ti−(coronene)$_2$ does not have different spectra when the vaporization laser timings are changed. It has a sharp onset peak near 1.5 eV under all conditions (spectra not shown). This species has almost the same EA as that of Ti−coronene. It is therefore tempting to conclude that Ti−(coronene)$_2$ exists primarily as an external metal isomer and not as a sandwich. V$_2$−(coronene)$_2$ is the only other potential sandwich species for which we are able to obtain PES spectra. It also exhibits a rather sharp onset (spectra not shown) near 1.5 eV under all conditions, perhaps indicating structures with at least one external metal. The structures and energetics of all of these potential isomeric structures for both vanadium and titanium analogues are clearly interesting issues that should be addressed by theory.

Conclusions

Anion complexes with multiple atoms of vanadium or titanium added to the PAH molecule coronene are produced by pulsed-nozzle laser vaporization methods. The anions are size-selected and studied with laser photoelectron spectroscopy in a magnetic bottle electron time-of-flight spectrometer. The electron affinity values measured for metal−coronene complexes are generally greater than those for the corresponding metal atom or metal cluster or for the free coronene molecule. The EA values increase with the number of metal atoms present, as has been observed previously for pure metal atom clusters. The V−(coronene)$_2$ complex exhibits two different spectra depending on the cluster source conditions. One of these has an EA value almost the same as the V−coronene complex, and this is assigned to an external-metal isomer. The prominent spectrum is then assigned to a sandwich isomer, which has a lower EA. It is clear that more structural isomers become possible as the number of metal atoms and coronene molecules increases, but interesting questions arise already in the small cluster sizes. It is not clear whether central or outer ring sites are preferred for metal binding, and it is not clear how additional metals add to the PAH surface. Although the PES spectra presented here are at relatively low resolution, they represent the first spectroscopic data of any kind on these metal−PAH complexes. Although the spectra do not determine structures directly, they do provide target numbers for EA values and state densities near threshold that can be tested with theory. When suitable calculations become available, it may thus be possible to confirm the tentative structural assignments proposed here.

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