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Seven-Coordinate Homoleptic Metal Carbonyls in the Gas Phase

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Received May 15, 2009; E-mail: maduncan@uga.edu

Stable metal carbonyls such as $Fe(CO)_5$ and $Cr(CO)_6$ are prototypical examples of the 18-electron rule in inorganic and organometallic chemistry.[1] Although seven-coordinate (7C) complexes are known for other ligands [e.g., ReF_7, $Mo(CN)_7^{5-}$],[2,3] homoleptic 7C carbonyls have not been characterized. Despite the odd shapes and steric crowding of these structures, they can be stable when the inclusion of a seventh ligand completes the 18-electron shell. The 7C carbonyls of the titanium-group metals would satisfy the 18-electron rule and could be stable.[4] Isovalent to neutral Ti complexes are those of the *cations* of the vanadium family (V^+, Nb^+, Ta^+). Theory has predicted that $V(CO)_7^+$ should be stable,[5] and collision induced dissociation experiments found the $V(CO)_6^+{-}CO$ bond energy to be greater than expected, indicating a possible 7C structure.[6] IR spectra of metal carbonyls provide a sensitive indicator of their structure and bonding.[7−9] However, there has been no spectroscopic confirmation of any homoleptic 7C metal carbonyl. We report here an IR spectroscopy study of the vanadium-group-cation carbonyls in the gas phase that reveals 7C structures for the Nb^+ and Ta^+ species but not for V^+.

The ion production and spectroscopy methods used here have been described previously.[10−13] Metal ion carbonyls were produced in a molecular beam by laser vaporization in a supersonic expansion of pure CO. Cations were mass-analyzed and size-selected in a reflectron time-of-flight spectrometer. The density of selected ions is too low for absorption measurements, so we employed IR photodissociation spectroscopy.[10] Excitation in the 2000−2300 cm^{-1} carbonyl-stretch region was done using the tunable output of a pulsed OPO/OPA laser system (LaserVision) pumped by a Nd:YAG laser (Spectra Physics Pro 230). Upon resonant IR absorption, the selected ion can fragment if the photon energy exceeds the energy of some bond in the cluster. The fragment ion yield as a function of the wavelength provides the IR spectrum. To support this work, DFT calculations were carried out using the uB3LYP functional in pc-GAMESS.[14] The DZP basis set was used for C and O, while the Wachters primitive basis set augmented with two p and one d function was used for V. The Stuttgart basis set with an effective core potential was used for Nb, and the Def2-QZVPP ECP basis set with the three most diffuse s functions removed was used for Ta.

Figure 1 shows the mass spectra of $V(CO)_n^+$ and $Ta(CO)_n^+$ ions containing 15−20 carbonyls. These include both strongly bound ligands coordinated to the metal and second-sphere species weakly bound to the exterior of the complex (formed only because of the cold supersonic beam conditions). The most abundant carbonyls for V and Ta are the $n = 6$ and 7 species, respectively, suggesting inherent stability for these complexes.[10,11] The insets show representative fragmentation data for $V(CO)_9^+$ and $Ta(CO)_9^+$ obtained by subtracting the laser-off mass spectrum of the selected ion from the laser-on one. The negative peaks show depletion of the parent ions through dissociation into fragment ions (positive peaks). The low energy of the IR photons used here can eliminate one or more external ligands but not those coordinated to the metal. Ligand elimination terminates at $n = 6$ for V and $n = 7$ for Ta, revealing the strongly bound core ions present. These are the same as the most abundant ions produced initially.

The IR spectra of the strongly bound core ions of $V(CO)_n^+$, $Nb(CO)_n^+$, and $Ta(CO)_n^+$ were obtained from the wavelength dependence of these fragmentation patterns, as shown in Figure 2. As discussed elsewhere,[11] the external CO ligands vibrate at a frequency (2165 cm^{-1} here) near that of free CO and have a negligible effect on the spectra of the core ions. DFT calculations confirmed this [see the Supporting Information (SI)]. For $V(CO)_n^+$, no complexes smaller than $n = 7$ fragment efficiently. $V(CO)_7^+$ fragments by losing one CO, producing the spectrum assigned to $V(CO)_6^+$ in Figure 2, which has one broad band at 2102 cm^{-1}. $V(CO)_8^+$ fragments by the loss of two COs, producing the same spectrum; apparently, no strongly bound $V(CO)_7^+$ ion was produced in this experiment. $Ta(CO)_n^+$ ions for $n < 8$ do not photodissociate. $Ta(CO)_8^+$ fragments by the loss of one CO to produce the spectrum attributed to $Ta(CO)_7^+$, which has five bands, clearly indicating lower symmetry. Surprisingly, $Nb(CO)_n^+$ produces different spectra in different fragmentation channels. $Nb(CO)_8^+$ loses two COs, producing a spectrum similar to that for $V(CO)_6^+$ (see the SI), but also loses one CO, producing a spectrum like that for $Ta(CO)_7^+$ (shown in Figure 2). The ratio of these channels is ∼1:1. Apparently, stable 6C and 7C species coexist for Nb^+.

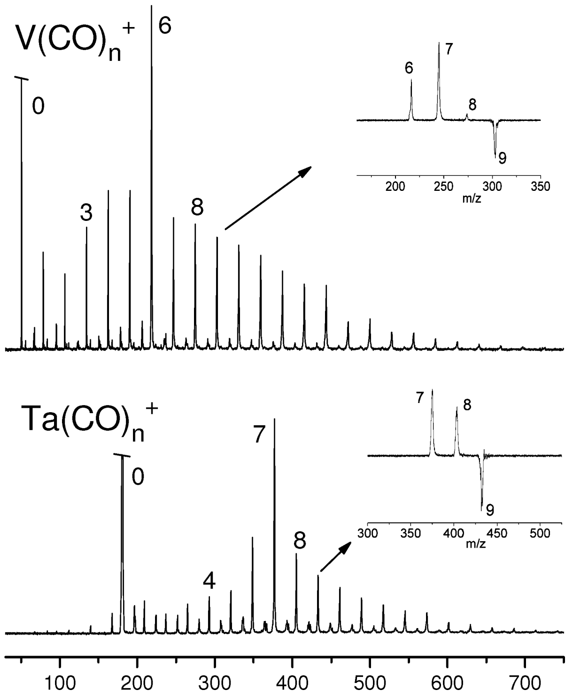

Figure 1. Mass spectra (atomic ion peaks off-scale) and IR photodissociation spectra.

DFT computations allowed us to confirm the stable structures present and to assign the bands in these spectra (see the SI for computed structures and IR spectra). Figure 2 shows computed spectra for the representative 6C $Nb(CO)_6^+$ and 7C $Nb(CO)_7^+$ ions. The lowest-energy isomer for each 6C complex was found to be the triplet with D_{3d} symmetry (slightly distorted from O_h symmetry because of the Jahn−Teller effect).[7,8] Thus, the expected spectrum has one main band, with closely spaced multiplet structure hidden at this resolution. The lowest-energy isomer for the 7C species is the singlet with a C_{3v} capped octahedral structure (*not* pentagonal

10.1021/ja903983u CCC: $40.75 © 2009 American Chemical Society

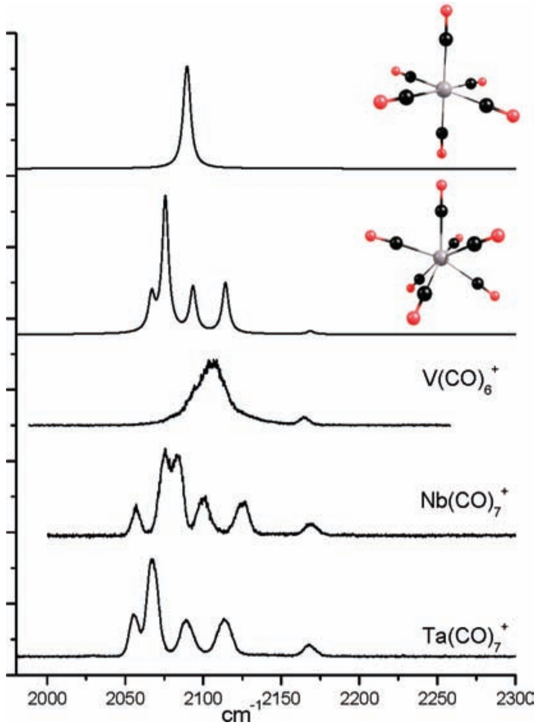

Figure 2. Calculated IR spectra of 6C Nb(CO)$_6^+$ and 7C Nb(CO)$_7^+$ complexes and experimental spectra of 6C V(CO)$_6^+$, 7C Nb(CO)$_7^+$, and 7C Ta(CO)$_7^+$. Computed frequencies were scaled by 0.94, and bands were given a 5 cm^{-1} fwhm Lorentzian line shape.

bipyramidal; see the SI). Because of the lower symmetry, five different carbonyl frequencies were predicted. The computed 6C spectrum is in good agreement with the experimental V(CO)$_6^+$ and Nb(CO)$_6^+$ spectra, while the computed 7C spectrum is in excellent agreement with those measured for Nb(CO)$_7^+$ and Ta(CO)$_7^+$. The differences between these computed and measured 6C and 7C spectra are quite compelling.

The peak at 2102 cm^{-1} for V(CO)$_6^+$ is assigned to unresolved nearly degenerate CO stretches of the D_{3d} core ion.[5] This band is ~100 cm^{-1} higher in frequency than that in the spectrum of the neutral 17-electron V(CO)$_6$ complex[15] and is closer to the free molecular CO stretch at 2143 cm^{-1}. The reduced red shift is attributed to decreased π back-bonding in the cation.[11] The spectrum of the Nb(CO)$_7^+$ complex from Nb(CO)$_8^+$ has five bands at 2057, 2075, 2100, 2125, and 2169 cm^{-1} assigned to the 7C species; the additional peak at 2083 cm^{-1} is from the overlapping spectrum of the 6C complex. This peak is also present as the main feature in the spectrum of Nb(CO)$_6^+$ measured by the loss of two COs from Nb(CO)$_8^+$. This again corresponds to a blue shift of ~100 cm^{-1} in the carbonyl stretch relative to 17-electron Nb(CO)$_6$.[16]

The spectrum of Ta(CO)$_7^+$ from Ta(CO)$_8^+$ shows no evidence of a 6C complex. The five bands at 2056, 2067, 2089, 2113, and 2168 cm^{-1} have the same pattern as for Nb(CO)$_7^+$ and are in excellent agreement with the computed pattern for the 7C complex. The weak 2168/2169 cm^{-1} bands for the 7C Ta$^+$ and Nb$^+$ complexes are near the frequency of the external CO in the 6C species but are computed for the 7C complexes. Therefore, V$^+$ forms only the 6C complex, Nb$^+$ both 6C and 7C species, and Ta$^+$ only the 7C one. The larger ions are apparently more able to accommodate the additional ligand. This trend is reflected in the computed energies (Table 1) for the 6C + 1 versus 7C structures for these metals, where the 7C has lower relative energy for the heavier metals. Presumably, both steric considerations and bond energies are at work here. Another consideration is that all the calculated 6C species are triplets, while the 7C complexes are singlets. If the spin change inhibits the last ligand addition, increased spin−orbit coupling in the heavier ions could overcome this more effectively. It is still surprising that no evidence for the 7C V(CO)$_7^+$ complex was found even though it is predicted to be the lower-energy isomer and was apparently seen previously.[6] However, the energetics of different spin states in metal complexes are often misjudged by DFT/B3LYP calculations,[17] and thus, the computed electronic energies may not be completely reliable. Additional studies using other functionals and basis sets may better elucidate these trends. If energy or spin activation barriers influence the last ligand addition, then the colder ion growth here than in the previous study[6] might explain why 7C V(CO)$_7^+$ was not seen. To further test our conclusions, we studied these 6C and 7C complexes with "argon tagging" photodissociation spectroscopy, in which the spectrum of each M(CO)$_n^+$ was measured by the elimination of argon from M(CO)$_n^+$−Ar.[10] The band positions and coordination patterns reported here were confirmed in every case by this method.[18]

Table 1. Relative Energetics (kcal/mol) for the 7C and 6C + 1 Metal Carbonyl Complexes

ion	7C	6C + 1
V(CO)$_7^+$	0.0	7.2
Nb(CO)$_7^+$	0.0	25.1
Ta(CO)$_7^+$	0.0	30.2

These gas-phase measurements have provided the first spectroscopic evidence for 7C homoleptic metal carbonyls. For the vanadium-group cations, 7C complexes were found for Nb$^+$ and Ta$^+$ but not for V$^+$. These complexes have a C_{3v} capped octahedral structure. The findings are more varied than expected on the basis of either the 18-electron rule or DFT. The vanadium-group carbonyls can provide a useful benchmark for the performance of different DFT functionals and may eventually reveal the subtle interplay of factors (size, spin, bond strength, growth dynamics) that make heptacoordination possible.

Acknowledgment. We gratefully acknowledge support of this work from the U.S. DOE (Grant DE-FG02-96ER14658) and the AFOSR (Grant FA95509-1-0166).

Supporting Information Available: Computational details and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA903983U