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Carbon dioxide is tightly bound in the [Co(Pyridine)(CO₂)]⁻ anionic complex

Jacob D. Graham,¹ Allyson M. Buytendyk,¹ Xinxing Zhang,¹ Seong K. Kim,² and Kit H. Bowen^{1,a)}

¹Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA

²Department of Chemistry, Seoul National University, Seoul 151-747, South Korea

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The [Co(Pyridine)(CO₂)]⁻ anionic complex was studied through the combination of photoelectron spectroscopy and density functional theory calculations. This complex was envisioned as a primitive model system for studying CO₂ binding to negatively charged sites in metal organic frameworks. The vertical detachment energy (VDE) measured via the photoelectron spectrum is 2.7 eV. Our calculations imply a structure for [Co(Pyridine)(CO₂)]⁻ in which a central cobalt atom is bound to pyridine and CO₂ moieties on either sides. This structure was validated by acceptable agreement between the calculated and measured VDE values. Based on our calculations, we found CO₂ to be bound within the anionic complex by 1.4 eV. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935573>]

INTRODUCTION

After Kim and co-workers first established that the addition of an excess electron induces covalent bonding in the pyridine(CO₂) complex,¹ subsequent work provided strong evidence of covalent bonding in other negatively charged complexes composed of CO₂ and the heterocyclic nitrogen molecules: pyrazine, pyridazine, pyrimidine, triazine, and 2-aminopyridine.^{2,3} In addition, we recently⁴ examined the [quinoline(CO₂)]⁻ anionic complex using both photoelectron spectroscopy and density functional theory calculations and were able to determine that carbon dioxide is bound within that complex by 0.6 eV, i.e., by a binding energy which is comparable to that of a typical Lewis acid-base pair (adduct). Additionally, the excess electron was shown to be necessary for this bonding, since the neutral quinoline(CO₂) complex was found to be a weakly bound van der Waals complex.

Transition metals and CO₂ have also been found to interact strongly when excess negative charges are involved. Through infrared photodissociation studies, Knurr and Weber have surveyed a variety of M(CO₂)_n⁻ clusters. Their work with Ag(CO₂)_n⁻ and Au(CO₂)_n⁻ cluster anions^{5,6} found that they have strongly bound core ions of the form, M(CO₂)⁻, whereas their work with Co(CO₂)_n⁻ and Ni(CO₂)_n⁻ cluster anions found that those have tightly bound core ions of the form, M(CO₂)₂⁻.^{7,8}

Carbon dioxide capture by metal organic frameworks (MOFs) has attracted particular interest due to the extremely high surface areas and tunable properties of MOFs.⁹ Carbon dioxide adsorbs primarily onto open metal sites in MOFs. Since we know that an excess electron can induce strong bonding between CO₂ and some transition metal atoms as well as between CO₂ and N-heterocyclic molecules, and

since we have previously characterized the [Co(Pyridine)]⁻ dimeric anion,¹⁰ we have chosen to complete the picture by studying the [Co(Pyridine)(CO₂)]⁻ anionic complex as a primitive model for CO₂ binding to negatively charged sites in MOFs. In [Pyridine(CO₂)]⁻, the CO₂ binds to the nitrogen atom's lone pair, while in [Co(Pyridine)]⁻, the cobalt atom is positioned above the pyridine ring. Here, we are interested in exploring where and how strongly CO₂ is bound within the [Co(Pyridine)(CO₂)]⁻ complex. We have used the combination of anion photoelectron spectroscopy and density functional theory to shed light on these questions.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Anion photoelectron spectroscopy is conducted by crossing a beam of mass-selected negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our apparatus consists of a laser vaporization cluster anion source, a time-of-flight mass analyzer, a Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. The instrumental resolution of the photoelectron spectrometer is ~35 meV at a 1 eV EKE. The third (355 nm) harmonic of a Nd:YAG laser was used to photodetach electrons from mass-selected [Co(Pyridine)(CO₂)]⁻ anionic complexes. Photoelectron spectra were calibrated against the well-known atomic transitions of atomic Cu⁻.

The laser vaporization ion source used in this work consisted of a rotating and translating cobalt rod and a pulsed valve (pressurized with 4 bars of helium and 10% CO₂, seeded with pyridine vapor). To generate the cluster anions of interest, the cobalt rod was ablated with the second harmonic output of a Nd:YAG laser, while the pulsed valve provided

^{a)}Author to whom correspondence should be addressed. Electronic mail: kbowen@jhu.edu. Telephone: (410) 516-8425.

bursts of the pyridine/ CO_2 /helium gas mixture. This mixture of vaporized cobalt atoms, CO_2 , pyridine, and electrons interacted and cooled in the expanding helium jet, generating $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ anionic complexes, which next passed through a skimmer and into the time-of-flight mass spectrometer portion of the apparatus.

Density functional theory calculations were performed with the Gaussian 09 software package.¹¹ All calculations were carried out with the B3LYP functional^{12,13} and 6-31++G(2d,2p) basis set.¹⁴ The B3LYP functional was found to be satisfactory during Knurr and Weber study of $[\text{Co}(\text{CO}_2)_n]^-$.⁷ For the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ anion, ten different starting geometries were optimized, these having different spin states and various placements of cobalt, CO_2 , and pyridine. This was done without symmetry constraints and using default convergence parameters. Most starting geometries converged to a few generally similar geometries. Frequency analyses were performed to confirm the identification of stationary points and to provide zero-point energies. Vertical detachment energies were computed from the energetic difference between a given geometrically relaxed anionic complex and its corresponding neutral species at the geometry of the relaxed anion. Natural population analysis was used to determine the partial charge of the cobalt, the CO_2 , and the pyridine moieties within the larger anionic complex. Dissociation energies were determined by subtracting the total energy of the bound anionic complex from the sum of the energies of the dissociated products.

RESULTS AND DISCUSSION

The anion photoelectron spectra of $[\text{Pyridine}(\text{CO}_2)]^-$, $[\text{Co}(\text{Pyridine})]^-$, $\text{Co}(\text{CO}_2)^-$, and $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ are shown for comparison in Figure 1. While all of these spectra were measured on our apparatus with 355 nm photons, that of $[\text{Pyridine}(\text{CO}_2)]^-$ is Kim's original spectrum repeated,¹ that of $[\text{Co}(\text{Pyridine})]^-$ is a previously published spectrum of ours,¹⁰ that of $[\text{Co}(\text{CO}_2)]^-$ (vertical detachment energy (VDE) ~ 2.2 eV) is new, and that $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ is the (new) subject of this paper.

The photoelectron spectrum of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ consists of a single broad, vibrationally unresolved band that begins at ~ 2.0 eV EBE and exhibits a VDE value of 2.7 eV. The relatively high VDE value of the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ spectrum contrasts sharply with the VDE values of the $[\text{Co}(\text{Pyridine})]^-$ and $[\text{Pyridine}(\text{CO}_2)]^-$ spectra, i.e., at 1.2 eV and 1.4 eV, respectively. Anion-molecule solvation strengths (physisorption interactions) are typically ~ 0.1 - 0.2 eV, and the solvation of an anion by a single solvent molecule usually increases the VDE of the resultant solvated anion by that amount. The large VDE shift (1.5 eV) between the spectra of $[\text{Co}(\text{Pyridine})]^-$ and $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ indicates that CO_2 is not simply solvating $[\text{Co}(\text{Pyridine})]^-$; the CO_2 moiety is better described as having been chemisorbed. These same kinds of arguments rule out the solvation of $[\text{Pyridine}(\text{CO}_2)]^-$ by a cobalt atom. Also, while the VDE shift between the spectra of $[\text{Co}(\text{CO}_2)]^-$ and $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ is smaller at 0.5 eV, it is still too large to account for the

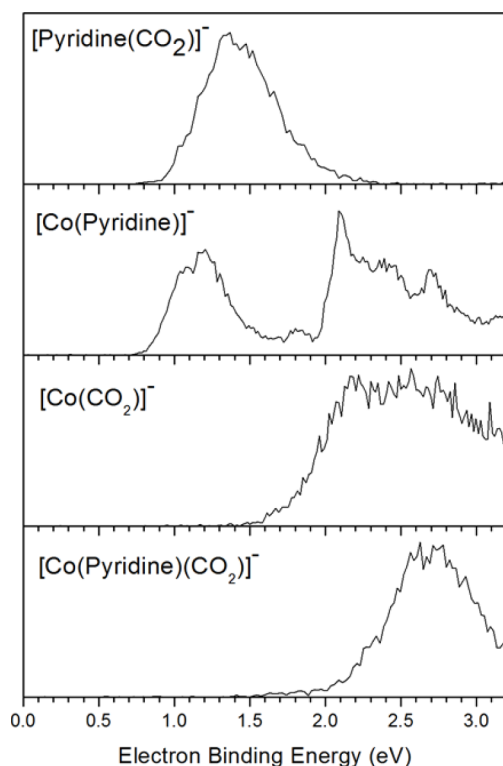


FIG. 1. Anion photoelectron spectra of $[\text{Pyridine}(\text{CO}_2)]^-$, $[\text{Co}(\text{Pyridine})]^-$, $[\text{Co}(\text{CO}_2)]^-$, and $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$.

solvation of $[\text{Co}(\text{CO}_2)]^-$ by pyridine. Again, a significantly stronger interaction than solvation must be present.

Geometries for $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ were identified computationally. The three lowest energy structures are labeled A–C in Figure 2. All of them are quite similar, with each structure exhibiting a central cobalt atom to which CO_2 and pyridine are bonded on opposite sides. The A structure has the lowest total energy, while structures B and C are only 0.09 eV and 0.20 eV higher in energy, respectively. The VDE values for structures A–C were calculated to be 2.05 eV, 1.79 eV, and 2.74 eV, respectively. Since the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ photoelectron spectrum has an energy threshold at ~ 2.0 eV, neither the calculated VDE value of structure A nor that of structure B is consistent with the measured VDE value. There is, in fact, very little photoelectron intensity in the spectrum at those calculated VDE values. The calculated VDE value of structure C, on the other hand, is in excellent agreement with the experimentally measured VDE value of 2.7 eV. Structure C, however, is slightly higher in energy (by ~ 0.1 eV) than structure B, and structure B is slightly higher in energy (by ~ 0.1 eV) than structure A. Still, these electronic energy differences are within the typical uncertainties of B3LYP. Thus, given how similar these three structures are both energetically and geometrically and given the agreement between the calculated VDE value of structure C and the experimentally determined VDE value, it seems likely that structure C is the actual structure of the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ anionic complex.

Structure C was further investigated by the application of natural population analysis. Partial charges were found to be

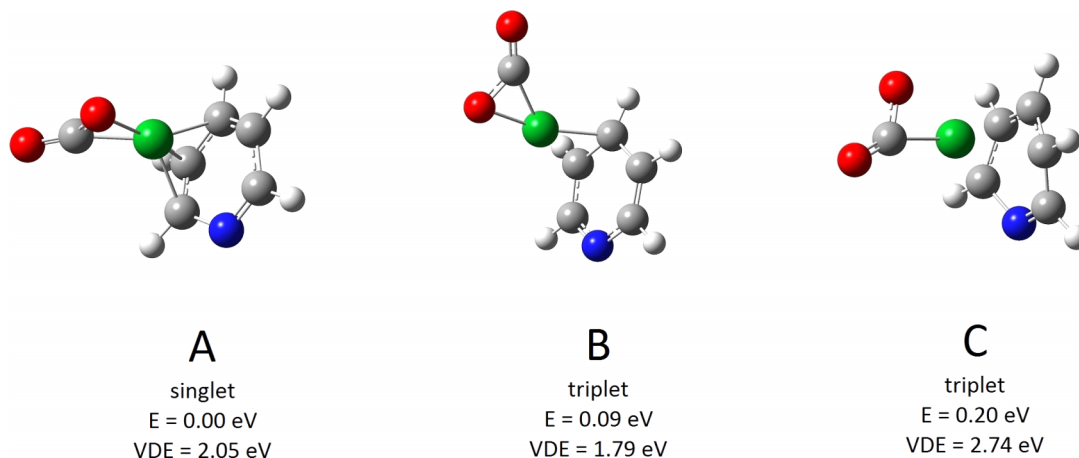


FIG. 2. Optimized anionic geometries of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$. Relative energies, VDE values, and spins are indicated. Carbon atoms are shown in grey, oxygen in red, cobalt in green, hydrogen in white, and nitrogen in blue.

+0.38 e on the Co atom, with pyridine and CO_2 exhibiting $-0.62 e$ and $-0.76 e$, respectively. This charge distribution suggests ionic bonding character. This charge distribution is similar to that found by Knurr and Weber⁷ for the $\text{Co}(\text{CO}_2)_2^-$ anion, where the central cobalt atom was positively charged and where the extremity CO_2 moieties were each negatively charged.

Three $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ (structure C) dissociation channels were investigated. These include the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ anionic complex dissociating into pyridine + $[\text{Co}(\text{CO}_2)]^-$, it dissociating into Co + $[\text{Pyridine}(\text{CO}_2)]^-$, and it dissociating into CO_2 + $[\text{Co}(\text{Pyridine})]^-$. Calculated values are presented in Table I. Based on these values, the pyridine moiety is seen to require the least energy (0.8 eV) to be removed from the anionic complex, while the cobalt atom moiety requires the most energy (1.7 eV) to be removed. At 1.4 eV, the energy to remove the CO_2 moiety from the anionic complex is intermediate between the other two.

There is a rough correlation between VDE differences (shifts) and dissociation energies. Consider the following energetic relationship:

$$\text{EA}[\text{XYZ}] + D_0[\text{XY} \dots \text{Z}] = \text{EA}[\text{XY}] + D_0[(\text{XY})^- \dots \text{Z}], \quad (1)$$

where $\text{EA}[\text{XYZ}]$ is the adiabatic electron affinity of XYZ, $\text{EA}[\text{XY}]$ is the adiabatic electron affinity of XY, $D_0[\text{XY} \dots \text{Z}]$ is the dissociation energy of neutral XYZ breaking into neutral XY and neutral Z, and $D_0[(\text{XY})^- \dots \text{Z}]$ is the dissociation energy of the anionic complex, $(\text{XYZ})^-$ breaking into anionic $(\text{XY})^-$ and neutral Z. Often, $D_0[(\text{XY})^- \dots \text{Z}]$ values are substantially larger than $D_0[\text{XY} \dots \text{Z}]$ values, in which case the following approximation holds:

$$\text{EA}[\text{XYZ}] - \text{EA}[\text{XY}] \sim D_0[(\text{XY})^- \dots \text{Z}]. \quad (2)$$

TABLE I. Calculated dissociation energies.

Dissociation pathway	D_0 (eV)
$[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{Pyridine} + \text{CoCO}_2^-$	0.8
$[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{Co} + \text{PyridineCO}_2^-$	1.7
$[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{CO}_2 + \text{CoPyridine}^-$	1.4

Note that $\text{VDE} = \text{EA} + \text{RE}$, where RE is the reorganizational energy, which itself is the difference between the energy of a relaxed neutral and the energy of that neutral when its structure is the same as that of its corresponding (relaxed) anion. If one substitutes $\text{VDE}[(\text{XYZ})^-] - \text{RE}[\text{XYZ}]$ for $\text{EA}[\text{XYZ}]$ and $\text{VDE}[(\text{XY})^-] - \text{RE}[\text{XY}]$ for $\text{EA}[\text{XY}]$ and makes the simplistic assumption that $\text{RE}[\text{XYZ}] \sim \text{RE}[\text{XY}]$, then a rough correlation should exist between the energy differences $\text{VDE}[(\text{XYZ})^-] - \text{VDE}[(\text{XY})^-]$ and $D_0[(\text{XY})^- \dots \text{Z}]$, i.e.,

$$\text{VDE}[(\text{XYZ})^-] - \text{VDE}[(\text{XY})^-] \sim D_0[(\text{XY})^- \dots \text{Z}]. \quad (3)$$

For the three dissociation energies calculated in this work, let us examine how well the above correlation holds, both qualitatively and quantitatively. In the case of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{pyridine} + [\text{Co}(\text{CO}_2)]^-$, the dissociation energy is 0.8 eV, while the difference between the measured VDE values of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ and $[\text{Co}(\text{CO}_2)]^-$ is 0.5 eV. Next, in the case of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{CO}_2 + [\text{Co}(\text{Pyridine})]^-$, the dissociation energy is 1.4 eV, while the difference between the measured VDE values of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ and $[\text{Co}(\text{Pyridine})]^-$ is 1.5 eV. Finally, in the case of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^- \rightarrow \text{Co} + [\text{Pyridine}(\text{CO}_2)]^-$, the dissociation energy is 1.7 eV, while the difference between the measured VDE values of $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ and $[\text{Pyridine}(\text{CO}_2)]^-$ is 1.3 eV. There is clearly some degree of correlation, although it is not thoroughgoing.

Through photoelectron measurements and DFT calculations, the $[\text{Co}(\text{Pyridine})(\text{CO}_2)]^-$ anionic complex is shown to have strong interactions among its moieties. In particular, the energy needed to remove CO_2 from the anionic complex was found to be 1.4 eV. This is quite substantial for CO_2 binding.

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