

Photoelectron spectroscopic study of the anionic transition metalorganic complexes $[\text{Fe}_{1,2}(\text{COT})]^-$ and $[\text{Co}(\text{COT})]^-$

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The gas-phase, iron and cobalt cyclooctatetraene cluster anions, $[\text{Fe}_{1,2}(\text{COT})]^-$ and $[\text{Co}(\text{COT})]^-$, were generated using a laser vaporization source and studied using mass spectrometry and anion photoelectron spectroscopy. Density functional theory was employed to compute the structures and spin multiplicities of these cluster anions as well as those of their corresponding neutrals. Both experimental and theoretically predicted electron affinities and photodetachment transition energies are in good agreement, authenticating the structures and spin multiplicities predicted by theory. The implied spin magnetic moments of these systems suggest that $[\text{Fe}(\text{COT})]$, $[\text{Fe}_2(\text{COT})]$, and $[\text{Co}(\text{COT})]$ retain the magnetic moments of the Fe atom, the Fe_2 dimer, and the Co atom, respectively. Thus, the interaction of these transition metal, atomic and dimeric moieties with a COT molecule does not quench their magnetic moments, leading to the possibility that these combinations may be useful in forming novel magnetic materials. © 2008 American Institute of Physics. [DOI: 10.1063/1.2977980]

I. INTRODUCTION

Over fifty years ago the synthesis of ferrocene¹ and dibenzene chromium² prompted a revolution in organometallic chemistry. In more recent times, both experiment and theory have explored gas-phase, transition metalorganic complexes with benzene,^{3–22} pyridine,²³ fullerenes,^{7,22,24–32} various polycyclic aromatic hydrocarbons (PAHs),^{7,33–42} and 1,3,5,7-cyclooctatetraene⁴³ (COT) serving as organic moieties. These studies provide information regarding the interactions between the *d* electrons of transition metals and the π electrons of organic molecules. In order to maintain the high magnetic moments of transition metal atoms and small clusters residing on or in organic molecular surfaces, it is important to identify transition metal-organic systems in which the organic moieties do not quench the metals' magnetic moments, but instead serve to protect them. Toward this end, we have previously investigated the structural, electronic and magnetic properties of several transition metal-organic systems using both experimental and theoretical methods.^{11,15,16,23,42} Here, we add to these studies by reporting on our work with iron and cobalt cyclooctatetraene cluster anions, $[\text{Fe}_{1,2}(\text{COT})]^-$ and $[\text{Co}(\text{COT})]^-$, using mass spectrometry, anion photoelectron spectroscopy, and density functional theory computations.

Cyclooctatetraene (COT) is a planar, cyclic molecule with eight π electrons. While COT bears a structural resemblance to benzene, which is of course aromatic, COT is anti aromatic. (Recall that while $4n+2$ π electrons are required for aromaticity, $4n$ π electrons lead to antiaromaticity.) Uranocene was the first metal-COT sandwich complex to be

discovered.⁴⁴ The structure of uranocene is analogous to ferrocene, with two COT molecules sandwiching a uranium atom. The stabilities of both ferrocene and uranocene are attributed to charge transfer from the metal atom to their neighboring organic moieties, such that they become aromatic. In uranocene, uranium donates two electrons to each COT molecule creating two, ten π electron (and thus aromatic) COT dianions and an U^{4+} core.

There have been several gas-phase studies of metal-COT complexes. Kaya, Nakajima, and co-workers^{22,45–49} generated cationic complexes of lanthanide metals with COT and recorded their mass spectra. From their observation that $[\text{Ln}_n(\text{COT})_{n+1}]^+$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Ho}, \text{Yb}$) cluster cations exhibited especially strong intensities, they concluded that these stoichiometries are exceptionally stable, and that they result from the formation of multiple decker sandwich structures with strong ionic interactions between the lanthanide atoms and the COT rings. Scott *et al.*⁵⁰ also studied $[\text{Ln}_n(\text{COT})_m]^+$ ($\text{Ln}=\text{Sm}, \text{Dy}, \text{Nd}$) cationic complexes, in their case by photodissociation. They proposed that these clusters also adopt sandwich and multiple decker sandwich structures. In addition, Jaeger and Duncan⁴³ performed photodissociation studies on $[\text{M}(\text{COT})_{1,2}]^+$ ($\text{M}=\text{V}, \text{Fe}, \text{Ni}, \text{and Ag}$) cationic clusters. Bonding in transition metal-COT complexes involves more covalent character than in lanthanide metal-COT complexes.

II. EXPERIMENTAL

A laser vaporization source was used to produce the gas-phase $[\text{Fe}(\text{COT})]^-$, $[\text{Fe}_2(\text{COT})]^-$, and $[\text{Co}(\text{COT})]^-$ clusters. A rotating, translating iron or cobalt rod was ablated with the second harmonic (532 nm) of a pulsed Nd:YAG laser with a power of approximately 10 mJ per pulse. Nearby, a pulse of

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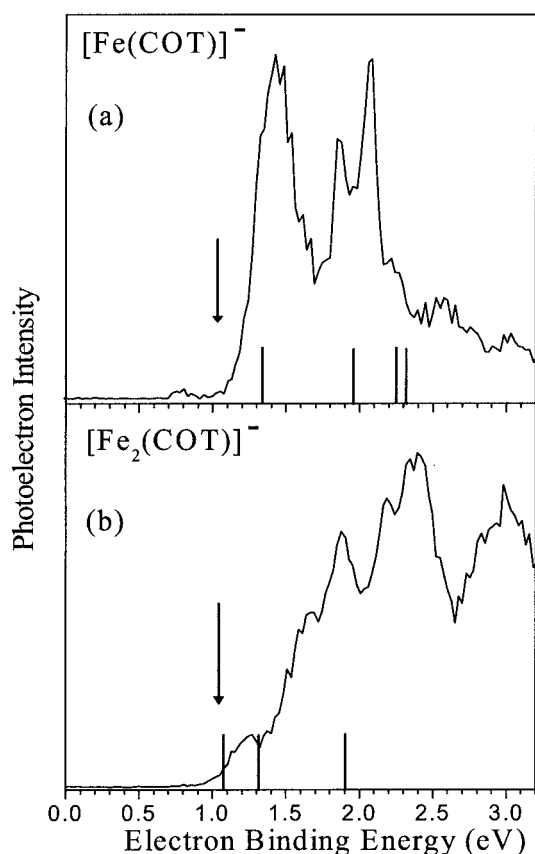


FIG. 1. The photoelectron spectra of $[\text{Fe}(\text{COT})]^-$ and $[\text{Fe}_2(\text{COT})]^-$ measured with 3.491 eV photons. The arrows indicate the calculated EA of the corresponding $\text{Fe}(\text{COT})$ and $\text{Fe}_2(\text{COT})$ neutrals. The sticks mark the calculated photodetachment transitions from two anionic isomers in each case.

helium (~ 4 atm) seeded with COT vapor was expanded from a pulsed valve. The anionic clusters were then mass analyzed and selected by a linear time-of-flight mass spectrometer (mass resolution of ~ 600). The third harmonic (355 nm, photon energy of 3.493 eV) of another Nd:YAG laser was used to photodetach the cluster anions of interest and a magnetic bottle photoelectron spectrometer was used for electron energy analysis. Negative ion photoelectron spectroscopy is governed by the energy-conserving relationship $h\nu = \text{EKE} + \text{EBE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. The details of our apparatus have been described previously elsewhere.¹¹

III. COMPUTATIONAL

Calculations were performed at the UMPW1PW91/6-31+G(*d,p*) level of theory. Geometry optimizations were performed with unconstrained symmetry in all cases. Global minimum energies for both the anion and the corresponding neutral species were determined by optimizing the geometries at several spin multiplicities. Adiabatic electron affinities were then taken as the energy difference between the lowest energy (geometry optimized) neutrals and the lowest energy (geometry optimized) anion isomers. Photodetachment transition energies were computed as the difference between the energy of the lowest energy

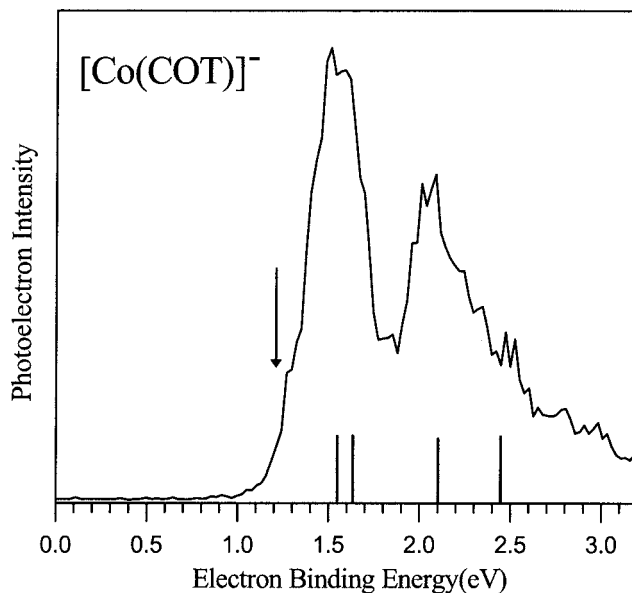


FIG. 2. The photoelectron spectrum of $[\text{Co}(\text{COT})]^-$ measured with 3.491 eV photons. The arrow indicates the calculated EA of the corresponding $\text{Co}(\text{COT})$ neutral. The sticks mark the calculated photodetachment transitions from two anionic isomers.

geometry of the anion (global minimum or higher in the case of some isomers) and the energies of the various neutral states each at the geometry of the anion. These were vertical, Δ (spin multiplicity) = ± 1 transitions in which the geometries of the neutrals were not optimized. All calculations were performed using GAUSSIAN03⁵³ and visualized with CHEMCRAFT.⁵⁴ The accuracy of the above mentioned theoretical method and basis set in identifying the ground state geometry, spectroscopic constants, and binding energies of neutral and cationic Fe-organic complexes has been well established.^{55,56} We tested the reliability of these modeling elements for anionic systems by calculating the EA values of Fe, Fe_2 , Co, and COT. Our calculated EA values of Fe, Fe_2 , Co, and COT (0.45, 1.04, 0.83, and 0.78 eV, respectively) are in reasonable agreement with the corresponding experimental values of 0.151,⁵¹ 0.902,⁵¹ 0.663,⁵⁷ and 0.55 eV (Ref. 58) (maximum deviation of 0.3 eV). Thus, the level of agreement obtained between our calculated results and the experimental values also establishes the reliability of our theoretical method for anionic Fe-organic complexes.

IV. RESULTS AND DISCUSSION

In the mass spectra of iron/COT and cobalt/COT cluster anions, the ion intensities of $[\text{Fe}(\text{COT})]^-$, $[\text{Fe}_2(\text{COT})]^-$, and $[\text{Co}(\text{COT})]^-$ clusters were weaker than the signal of the parent cyclooctatetraene anion itself. COT has a positive electron affinity, and our photoelectron spectrum of COT^- is consistent with the spectrum published previously by Lineberger.⁵¹ During the course of the experiment, no species containing more than one COT molecule were observed.

The photoelectron spectra of $[\text{Fe}(\text{COT})]^-$, $[\text{Fe}_2(\text{COT})]^-$, and $[\text{Co}(\text{COT})]^-$ are shown in Figs. 1 and 2. The adiabatic electron affinity (EA) of a cluster's corresponding neutral is defined as the energy difference between the anion and neutral both in their optimized ground state geometries. Electron

TABLE I. Experimental and theoretical electron affinities, photodetachment transitions and spin multiplicities for the $\text{Fe}_{1,2}(\text{COT})/[\text{Fe}_{1,2}(\text{COT})]^-$ and $\text{Co}(\text{COT})/[\text{Co}(\text{COT})]^-$ systems. The spin multiplicities refer to those of the neutrals' ground states.

| | Electron Affinity (eV) | | Photodetachment transitions (eV) | | Spin multiplicity (2S+1) |
|-----------------------|------------------------|-------|----------------------------------|-----------|--------------------------|
| | Expt. | Theo. | Expt. | Theo. | Theo. |
| Fe(COT) | 1.18 | 1.04 | 1.40 | 1.33 | 5 |
| | | | 1.88 | 1.97 | |
| | | | 2.08 | 2.21 | |
| | | | 2.20 | 2.32 | |
| Fe ₂ (COT) | 1.10 | 1.05 | 1.27 | 1.08 | 7 |
| | | | 1.65 | 1.31 | |
| | | | 1.88 | 1.91,1.91 | |
| | | | 2.18 | | |
| Co(COT) | 1.20 | 1.22 | 1.52 | 1.53 | 4 |
| | | | 1.61 | 1.63 | |
| | | | 2.06 | 2.10 | |
| | | | 2.49 | 2.44 | |

The uncertainty in experimental EA values ± 0.10 eV.

affinity values were estimated as the EBE at the onset of photodetachment intensity, shifted up in EBE slightly to account for typical vibrational hot band contributions. This corresponds to the EBE of the intensity maximum in the first (lowest EBE) peak in the photoelectron spectra. The peaks with higher binding energies correspond to vertical transitions from the ground state of the anion to various excited states of the neutral. Experimentally and theoretically determined electron affinities and photodetachment transition energies as well as theoretically determined spin multiplicities are shown in Table I.

A. $[\text{Fe}(\text{COT})]^-$ and Fe(COT)

The photoelectron spectrum of $[\text{Fe}(\text{COT})]^-$ is shown in Fig. 1(a). The EA of Fe(COT) is estimated to be 1.18 ± 0.10 eV using the methodology described above. The lowest EBE major peak is centered at 1.40 eV. Two additional transitions are observed at 1.88 and 2.08 eV. Several weaker features also exist at higher EBE values, starting with one at 2.2 eV.

Our calculations found two nearly degenerate isomers of $[\text{Fe}(\text{COT})]^-$. The most stable isomer of this anion [Fig. 3(a)] is a sextet exhibiting a C_{8v} structure with its iron atom sitting (centered) above the COT ring. The calculated first two photodetachment transitions from this isomer to its neutral quintet and septet states are predicted to be at EBE=1.33 and 2.32 eV, respectively. The other isomer is also a sextet but with C_s symmetry [Fig. 3(b)], and it is only 0.11 eV higher in energy than the lower energy isomer. In this isomer, the iron atom also sits on top of the COT molecule but in this case slightly off center. The different position of the iron atom in this isomer causes a slightly distorted geometry for the COT ring. The calculated first two transitions from this isomer to its neutral quintet and septet states are predicted to occur at EBE=1.97 and 2.21 eV, respectively. By comparison with our measured spectrum, it appears that the ground

state, anionic isomer contributes to the first (lowest EBE) and fourth (highest EBE) peaks in the photoelectron spectrum, while the second isomer contributes to the second and third peaks, i.e., both anionic isomers are present in the beam and both contribute to the photoelectron spectrum. The structure of the most stable neutral Fe(COT) is very close to that of its ground state anion [Fig. 3(c)]. The EA is calculated to be 1.04 eV, which is in good agreement with the experimental result of 1.18 eV.

The magnetic moment of the iron atom ($4\mu_B$) is significantly larger than iron's bulk magnetic moment of $2.2\mu_B$. If the relatively high magnetic moment present in the iron atom can be retained upon its interaction with COT, then the iron atom/COT molecule combination may be useful in forming novel magnetic materials, these, of course, corresponding to ground state, neutral systems. The theoretically predicted multiplicity of 5 for Fe(COT)'s neutral, ground state is supported by the match between the predicted and measured

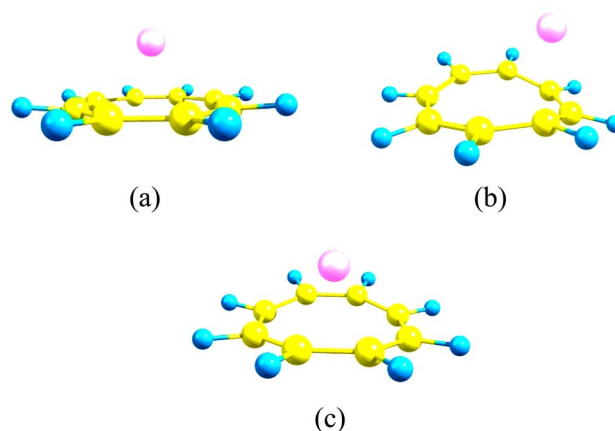


FIG. 3. (Color online) The calculated structures of anionic $[\text{Fe}(\text{COT})]^-$ and neutral Fe(COT). (a) The most stable isomer of $[\text{Fe}(\text{COT})]^-$. (b) The second most stable isomer of $[\text{Fe}(\text{COT})]^-$. (c) The ground state structure of neutral Fe(COT).

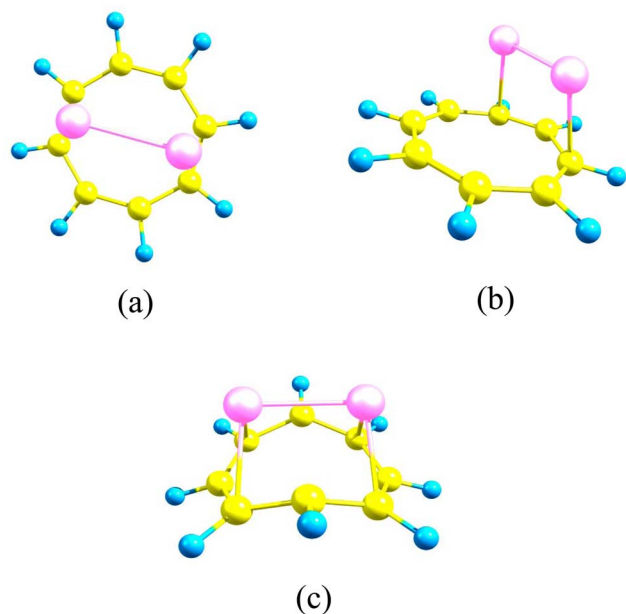


FIG. 4. (Color online) The calculated structures of anionic $[\text{Fe}_2(\text{COT})]^-$ and neutral $\text{Fe}_2(\text{COT})$. (a) The most stable isomer of $[\text{Fe}_2(\text{COT})]^-$. (b) The second most stable isomer of $[\text{Fe}_2(\text{COT})]^-$. (c) The ground state structure of neutral $\text{Fe}_2(\text{COT})$.

photodetachment transitions in the photoelectron spectrum of $[\text{Fe}(\text{COT})]^-$. This implies that the spin magnetic moment of the neutral $\text{Fe}(\text{COT})$ complex is $4\mu_B$. While this value is not the total magnetic moment—it does not include the orbital magnetic moment—orbital moments are usually small compared to spin magnetic moments in solids.⁵⁹ If so in this case, the magnetic moment of neutral ground state $\text{Fe}(\text{COT})$ is comparable to that of an iron atom and is significantly higher than the magnetic moment of bulk iron. Thus, the magnetic moment of the iron atom appears to be retained within the $\text{Fe}(\text{COT})$ complex as a whole.

B. $[\text{Fe}_2(\text{COT})]^-$ and $\text{Fe}_2(\text{COT})$

The photoelectron spectrum of $[\text{Fe}_2(\text{COT})]^-$ is presented in Fig. 1(b). A small peak is centered at $\text{EBE}=1.27$ eV, followed by several stronger peaks centered at 1.65, 1.88, and 2.18 eV. Two very strong, broad bands are also present at ~ 2.3 and ~ 3.0 eV. The EA of $\text{Fe}_2(\text{COT})$ was estimated to be 1.10 ± 0.10 eV, again using the methodology described above.

Our calculations found the structure of the lowest energy isomer of anionic $[\text{Fe}_2(\text{COT})]^-$ to consist of an iron dimer whose axis is parallel to the plane of the COT molecule, and whose projection bisects the COT ring; see [Fig. 4(a)]. The bond distance between the two iron atoms is 2.37 Å. The second most stable isomer, which is only 0.04 eV higher in energy, was found to consist of an iron dimer whose axis is also parallel to the plane of the COT molecule, but which sits off center, see [Fig. 4(b)]. The bond length of iron dimer in this isomer is 2.31 Å. In neutral $\text{Fe}_2(\text{COT})$, an iron dimer (bond length=2.31 Å) sits on top of a COT molecule which is bent away from the dimer; see Fig. 4(c). Photodetachment transitions from the lowest energy isomer of anionic $[\text{Fe}_2(\text{COT})]^-$, which is an octet, to neutral $\text{Fe}_2(\text{COT})$ states

of multiplicity 7 and 9, are predicted to occur at $\text{EBE}=1.08$ and 1.91 eV, respectively. Likewise, transitions from the higher energy anionic isomer, which is also an octet, to neutral $\text{Fe}_2(\text{COT})$ states of multiplicity 7 and 9, are predicted to occur at $\text{EBE}=1.31$ and 1.91 eV, respectively. These predicted transitions are marked on the $[\text{Fe}_2(\text{COT})]^-$ spectrum in Fig. 1(b). Since agreement between these predictions and the spectrum is reasonably good, it is likely that both anionic isomers are again contributing to the spectrum. Furthermore, the calculated EA of 1.05 eV is in excellent agreement with the experimental value of 1.10 eV.

A comparison between the photoelectron spectra and the geometric structures of $[\text{Fe}_2(\text{COT})]^-$ versus $[\text{Fe}_2(\text{coronene})]^-$ is interesting. While the axis of the iron dimer moiety is parallel to the plane of the organic molecule in $[\text{Fe}_2(\text{COT})]^-$, it is perpendicular in $[\text{Fe}_2(\text{coronene})]^-$. Likewise, their photoelectron spectral profiles are also very different. Furthermore, the photoelectron spectral profiles of $[\text{Fe}_2(\text{benzene})]^-$ and $[\text{Fe}_2(\text{pyrene})]^-$ are quite similar both to each other and to that of $[\text{Fe}_2(\text{coronene})]^-$,^{52,60,61} suggesting at least a broad degree of structural similarity between these three. We speculate that these relationships trace back to the aromaticity of benzene, pyrene, and coronene versus the antiaromaticity of COT.

The theoretically predicted multiplicity of 7 for $\text{Fe}_2(\text{COT})$'s neutral, ground state is supported by satisfactory agreement between the predicted and measured photodetachment transitions in the photoelectron spectrum of $[\text{Fe}_2(\text{COT})]^-$. This implies that the spin magnetic moment of neutral $\text{Fe}_2(\text{COT})$ is $6\mu_B$. The magnetic moment for Fe_2 is also $6\mu_B$. Assuming that the orbital magnetic moment in $\text{Fe}_2(\text{COT})$ is small, the magnetic moment of Fe_2 appears to be retained within the $\text{Fe}_2(\text{COT})$ complex as a whole, although the moment per iron atom is not necessarily $3\mu_B$ per atom. In any case, this suggests that the Fe_2/COT molecule combination may be useful in forming novel magnetic materials.

C. $[\text{Co}(\text{COT})]^-$ and $\text{Co}(\text{COT})$

The photoelectron spectrum of $[\text{Co}(\text{COT})]^-$ is presented in Fig. 2. The first of three major features covers the energy range from $\text{EBE}=1.2$ to 1.8 eV and is centered at 1.52 eV. The second feature covers the range from $\text{EBE}=1.9$ to 2.3 eV and is centered at 2.1 eV, while the third much weaker feature is centered at ~ 2.5 eV. The electron affinity of neutral $\text{Co}(\text{COT})$ ions estimated to be 1.20 eV. Our calculations found two degenerate structures for $[\text{Co}(\text{COT})]^-$ which differ by only 0.06 eV in energy [see Figs. 5(a) and 5(b)]. Both isomers prefer a structure with the cobalt atom binding to two carbon atoms on the edge of the COT ring. There are slight differences between them in terms of the relative positions of the cobalt atom and the COT molecule as well as in the bending of the COT molecule. Photodetachment transitions from the lowest energy isomer of anionic $[\text{Co}(\text{COT})]^-$, which is a quintet, to neutral $\text{Co}(\text{COT})$ states of multiplicity 4 and 6, are predicted to occur at $\text{EBE}=1.53$ and 2.44 eV, respectively. Likewise, transitions from the higher energy anionic isomer, which is also

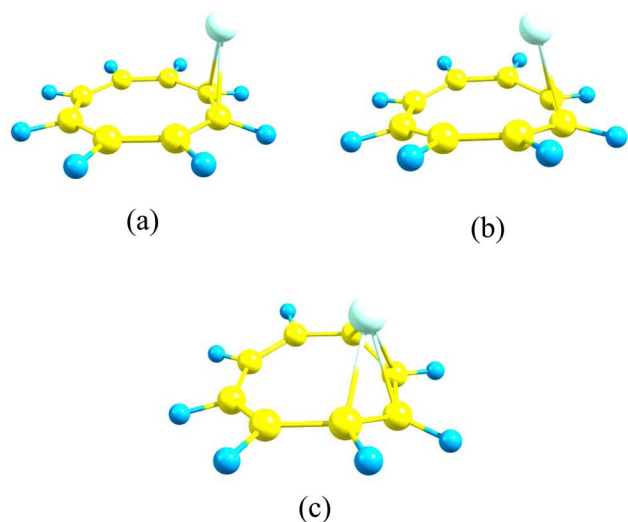


FIG. 5. (Color online) The calculated structures of anionic $[\text{Co}(\text{COT})]^-$ and neutral $\text{Co}(\text{COT})$. (a) The most stable isomer of $[\text{Co}(\text{COT})]^-$. (b) The second most stable isomer of $[\text{Co}(\text{COT})]^-$. (c) The ground state structure of neutral $\text{Co}(\text{COT})$.

a quintet, to neutral $\text{Co}(\text{COT})$ states of multiplicity 4 and 6, are predicted to occur at $\text{EBE}=1.63$ and 2.10 eV, respectively. These predicted transitions are marked on the $[\text{Co}(\text{COT})]^-$ spectrum in Fig. 2. Since agreement between these predictions and the spectrum is good, it is likely that both anionic isomers are again contributing to the spectrum. The structure of the most stable $\text{Co}(\text{COT})$ neutral is very close to that of the global minimum anion structure but with the cobalt atom sitting slightly closer to the center of the COT molecule [see Fig. 5(c)]. The calculated EA of 1.22 eV is in excellent agreement with the experimental value of 1.20 eV. Furthermore, the spectral profile of $[\text{Co}(\text{COT})]^-$ is quite similar to that of $[\text{Fe}(\text{COT})]^-$, suggesting that they and their neutral counterparts may have the same structures. It is, however, instructive to see the extent to which this expectation holds. A comparison of their calculated structures in Figs. 3 and 5 shows that, while they are indeed similar in broad terms, they are not identical.

The magnetic moment of the free cobalt atom ($3\mu_B$) is significantly larger than cobalt's bulk magnetic moment of $1.7\mu_B$. The theoretically predicted multiplicity of 4 for $\text{Co}(\text{COT})$'s neutral, ground state is supported by the agreement between the predicted and measured photodetachment transitions in the photoelectron spectrum of $[\text{Co}(\text{COT})]^-$. This implies that the spin magnetic moment of the neutral $\text{Co}(\text{COT})$ complex is $3\mu_B$. This implies that the magnetic moment of neutral ground state $\text{Co}(\text{COT})$ is comparable to that of an cobalt atom, and that the magnetic moment of the cobalt atom is retained within the $\text{Co}(\text{COT})$ complex.

Thus, the magnetic moments of all three metal moieties in the complexes, $\text{Fe}(\text{COT})$, $\text{Co}(\text{COT})$, and $\text{Fe}_2(\text{COT})$ are retained in their complexes. However, a comparison of metal-coronene complexes with the same metal moieties gives mixed results. For example, the magnetic moment of the cobalt atom is not retained in the $\text{Co}(\text{coronene})$ complex.⁴² While on the other hand, the magnetic moments of both the iron atom and the iron dimer are retained in the

complexes, $\text{Fe}(\text{coronene})$ and $\text{Fe}_2(\text{coronene})$.⁵² This serves to remind us of the complexity of the interactions within these systems, even when they appear to be relatively simple.

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