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Experimental evaluation of the stabilization of the COT orbitals by 4f orbitals in COT_2Ce using a Hubbard model

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Significant orbital mixing is rare in lanthanide complexes because of the limited radial extent of the 4f orbitals, which results in a generally small stabilization due to 4f orbital interactions. Nevertheless, even a small amount of additional stabilization could enhance lanthanide separations. One lanthanide complex in which orbital mixing has been extensively studied both experimentally and computationally is cerocene, COT_2Ce, where COT is cyclooctatetraene. This compound has a singlet ground state with a low-lying, triplet excited state. Previous fluorescence studies on trimethylsilyl-substituted cerocenes indicate the triplet state is 0.4 eV higher in energy than the singlet state. In addition, computational studies predict that the triplet is 0.3 to 1 eV higher in energy than the singlet. The synthesis of highly pure COT_2Ce by Walter and Andersen allowed its physical properties to be accurately measured. Using these measurements, we evaluate the stabilization of the 4f orbitals using two, independent approaches. A Hubbard model is used to evaluate the stabilization of the ground state due to orbital mixing. This stabilization, which is also the singlet-triplet gap, is -0.29 eV using this model. This gap was also from the temperature independent paramagnetism of COT_2Ce, which yielded a value of -0.32 eV.

Introduction

Lanthanide complexes typically display little mixing between metal 4f and ligand orbitals due to the contracted nature of the 4f orbitals.[1, 2] Consequently, bonding in trivalent lanthanide complexes is predominantly ionic. This behaviour, along with their similar ionic radii, makes separating trivalent lanthanide ions from each other challenging.[3] Lanthanide separations could potentially be improved by increasing the strength of the interactions between ligands and lanthanide ions. Given the contracted nature of the 4f orbitals and the correspondingly weak overlap with ligand orbitals, the additional stabilization is likely to be modest.[2] However, even modest increases in stabilization can substantially enhance separation factors: a difference in energy of 1.4 kcal mol^{-1} results in a separation factor of 10, and a difference of 5.5 kcal mol^{-1} already yields a separation factor of 10^4. Despite the relatively small amount of stabilization required to improve separations, no system has yet demonstrated improved separation of trivalent lanthanides because of orbital mixing, which underscores the challenges to such an approach. While orbital mixing in 4f complexes has not been used directly to improve lanthanide separations, enhanced stabilization due to greater overlap and stronger orbital mixing with the actinide 5f orbitals is believed to play an important role in the separation of actinides from lanthanides with similar ionic radii.[4-9]

A key factor in using orbital mixing to improve separation of trivalent lanthanides is the amount of stabilization that orbital mixing can introduce into an otherwise ionic complex. This quantity is challenging to evaluate both experimentally and computationally, but it has been determined spectroscopically to be 2.3 kcal mol^{-1} for $Cp^*_2Yb(bipy)$, where Cp* is pentamethylcyclopentadienyl, and bipy is 2,2'-bipyridyl.[10] A similar degree of orbital mixing was found in Cp_3Yb, where Cp is cyclopentadienyl, although the stabilization was not reported.[11, 12] In both Yb(III) complexes, the stabilization can be modelled by a configuration interaction (CI) that mixes a ligand to metal charge transfer (LMCT) state into the ground state. At the other end of the lanthanide series, both gas phase $[Cp_3Ce]^+$ and condensed phase cerocene (COT_2Ce, where COT is cyclooctatetraene), display analogous behaviour.[13-15] COT''_2Ce, where COT" is 1,4-bis-trimethylsilylcyclooctatetraene, has a singlet-triplet gap of 0.45 eV based on the luminescence studies by Amberger, et al.[16] As discussed below, the stabilization of the singlet state relative to the triplet state is the stabilization of the molecule as a result of 4f orbital mixing. The properties of COT''_2Ce and COT_2Ce are assumed to be similar. While COT''_2Ce

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has not be characterized crystallographically, the trimethylsilyl groups are not expected to greatly change the Ce – C distances relative to those in COT$_2$Ce. In the related Ce(III) anions, the Ce-COT(centroid) distance is only 0.02 Å longer in [COT"$_2$Ce]$^-$ relative to those of [COT$_2$Ce]$^-$, and the same is true for the U(IV) analogs of the cerocenes.[17-21] [COT"$_2$Ce]$^-$ and [COT$_2$Ce]$^-$ have oxidation potentials that differ by only 0.03 V, which suggests that replacing protons by trimethylsilyl groups does not strongly affect the electronic structures of the molecules.[18, 22]

The nature of the bonding in COT$_2$Ce has been the subject of vigorous discussion. The molecule has a singlet ground state and is a temperature independent paramagnet. Cerocene has been structurally characterized by single-crystal diffraction and EXAFS and has idealized D$_{8h}$ symmetry with little distortion.[23, 24] It was initially described as a Ce(IV) complex with two COT^{2-} ligands. This description was supported by the ionic radius analysis of Raymond and Eigenbrot.[25] Subsequent Xα calculations and photoelectron spectroscopic studies indicated a surprisingly large degree of 4f orbital involvement in bonding.[26] In a series of papers, Fulde, Dolg and co-workers suggested that COT$_2$Ce was better described as a Ce(III) compound with an electron localized on the Ce centre. As a result, there is a "hole" in the (COT^{2-})$_2$ ligand system, which can be described as COT$_2^{3-\bullet}$ or L^3, the latter of which indicates the presence of three electrons in the ligand orbitals. Crucially, the Ce 4f electron is coupled to an unpaired electron of L^3 forming an open-shell singlet ground state, $|4f^1L^3\rangle$.[27-31] Cerium K-edge X-ray absorption near edge structure (XANES) reported by Edelstein, et al. shows that COT"$_2$Ce features a spectrum similar to Ce(III) complexes, which supports the Fulde and Dolg description.[32] The categorization of COT$_2$Ce as a Ce(III) complex was further bolstered by luminescence studies of COT"$_2$Ce conducted by Amberger, et al., who determined that the first excited state was a triplet, which was 0.45 eV above the ground state.[16] The amount of 4f character in the ground state, n$_f$, was determined to be 0.89 for COT$_2$Ce by Booth, et al. using Ce L$_3$-edge XANES spectroscopy.[13] The ground state was further studied computationally by Katsoyannis, Kerridge, and coworkers.[33, 34] Recent results by Smiles, et al. unequivocally demonstrated significant orbital mixing between the Ce 4f and COT orbitals as shown by C K-edge XANES spectroscopy bolstered by extensive computational studies.[35] The calculated stabilization of the singlet state in COT$_2$Ce relative to the next state varies from 0.33 eV to 1.1 eV.[31, 34]

In addition to being difficult to model computationally, COT$_2$Ce has been challenging to synthesize. It was initially prepared by Greco, et al. via the reaction of cerium isopropoxide with triethylaluminium using cyclooctatetraene as the solvent.[36] An improved synthesis was reported by Streitwieser, et al., in which the Ce(III) anion, [COT$_2$Ce]$^-$, was oxidized by allyl bromide.[22] Trimethylsilyl-substituted cerocenes have been produced by a similar route (synthesis of the anionic, trivalent substituted-cerocene complex followed by oxidation to the neutral complex).[37] This approach was further refined by Andersen and Walter to prepare highly pure COT$_2$Ce, which enabled accurate determination of its magnetic susceptibility and Ce L$_3$ XANES spectrum.[38] These measurements serve as the benchmarks for computational models and are used for spectroscopic models to evaluate bonding in COT$_2$Ce. In this paper, the covalent stabilization of the COT$_2$Ce ground state is estimated from the measured properties using a Hubbard molecule model (HMM) and from its temperature independent paramagnetism.

Results

Hubbard molecule model (HMM) for COT$_2$Ce

The HMM was previously applied to Cp*$_2$Yb(bipy).[10] This model represents the simplest multi-electron model that accounts for electron correlation, which is particularly important for lanthanide and actinide ions where electron correlation is much stronger than orbital interactions. The basis for the HMM are the valence bonding states, which can be either ionic (M$^+$L$^-$ or M$^-$L$^+$), where electrons are localized on the metal or ligand, or covalent (M-L or M$^\bullet$ L$^\bullet$), in which electrons are shared between them. It should be noted that 'covalent' in this context does not imply a strong bonding interaction; it just indicates that the electrons are evenly shared. In the HMM, the singlet ground state is stabilized relative to the triplet state by a configuration interaction (CI) between an excited, charge-transfer state and the ground state. This interaction is analogous to orbital mixing in molecular orbital (MO) theory, and the stabilization of the ground state, E$_{GS}$, in the HMM is the stabilization as result of orbital mixing.[39-44] Spectroscopically, the amount of 4f character in the ground state of COT$_2$Ce is 0.89. Therefore, the unperturbed ground state in the HMM is $|4f^1L^3\rangle$. If the amount of 4f character in the ground state were less than 0.5, the unperturbed ground state would be $|4f^0L^4\rangle$.

To construct the HMM, we first need to identify the interacting states on Ce^{3+} and the ligands, COT$_2^{3-\bullet}$. The starting point is the MO description of the bonding, which has been investigated in detail most recently by Kerridge, et al. and Smiles, et al.[34, 35] The main bonding interaction between Ce and the COT ligands involves the Ce 4f$_\delta$ orbitals ($m_L = \pm 2$) and the doubly-degenerate e$_{2u}$ orbital of the ligands.[34] For COT$_2^{3-\bullet}$, the state used in the HMM is therefore E$_{2u}^3$. In the absence of spin-orbit coupling, the Ce 4f$_\delta$ orbital would be the other state. However, spin-orbit coupling is generally stronger than the crystal field and cannot treated as a perturbation as it is done in MO theory.

The ground state configuration of Ce^{3+} is 4f^1. Under Russell-Saunders coupling, this configuration has two terms. The ground state is $^2F_{5/2}$, and the excited state is $^2F_{7/2}$. Interactions with the two COT ligands (the crystal field) removes the spatial degeneracies of these terms, and the resulting states, $|J, m_J\rangle$, are described by the total angular momentum J and angular momentum quantum number m$_J$. These states are given in Table 1 in terms of 4f$_\sigma$, 4f$_\pi$, 4f$_\delta$, and 4f$_\phi$ and in Table S1 in terms of $|m_l, m_s\rangle$. In the D$_{8h}$ symmetry of COT$_2$Ce, the crystal field does not mix the m$_J$ states within a given term ($^2F_{5/2}$ or $^2F_{7/2}$).

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However, for a given value of m_J, the crystal field can mix the excited state term into the ground state. In other words, the |J=5/2, m_J=3/2⟩ state will contain a small amount of |7/2, 3/2⟩ character because of the crystal field. In $[COT_2Ce]^-$, only 2% of the |7/2, 1/2⟩ excited state is mixed into the |5/2, 1/2⟩ ground state,[38] and we assume that mixing of the excited J=7/2 states into the ground J=5/2 states is also small in COT_2Ce. The J=5/2 state with the most $4f_\delta$ character is |5/2, 3/2⟩. Therefore, in the HMM, the unpaired electron on Ce is assumed to be in the |5/2, 3/2⟩ state, and the three electrons on COT comprise the $E_{2u}{}^3$ state.

Table 1: |J, m_J⟩ states in terms of f_σ, f_π, f_δ, f_ϕ

|J, m_J⟩	
|7/2, 7/2⟩	f_ϕ
|7/2, 5/2⟩	1/7 f_ϕ+ 6/7 f_δ
|7/2, 3/2⟩	2/7 f_δ + 5/7 f_π
|7/2, 1/2⟩	3/7 f_π + 4/7 f_σ
|5/2, 5/2⟩	6/7 f_ϕ + 1/7 f_δ
|5/2, 3/2⟩	5/7 f_δ + 2/7 f_π
|5/2, 1/2⟩	4/7 f_π + 3/7 f_σ

Table 2: States Ψ_1 through Ψ_8 are combinations of the Ce $4f^1$ states and the $COT_2{}^{3-\bullet}$ states (electron spins are indicated by arrows)

	$4f^1$ |5/2, –3/2⟩ (↑)	$4f^1$ |5/2, +3/2⟩ (↓)
L^3 E_{2u} (↓)(↑↓)	Ψ_1	Ψ_5
L^3 E_{2u} (↑)(↑↓)	Ψ_2	Ψ_6
L^3 E_{2u} (↑↓)(↓)	Ψ_3	Ψ_7
L^3 E_{2u} (↑↓)(↑)	Ψ_4	Ψ_8
Ψ_9: $(COT^{2-})_2Ce$, |$4f^0L^4$⟩		

The HMM for COT_2Ce is constructed from nine different states, which are shown in Table 2. The eight lowest in energy, Ψ_1– Ψ_8, are the |$4f^1L^3$⟩ states. The ionic, formally Ce(IV) state corresponds to the excited, metal to ligand charge-transfer (MLCT) state, Ψ_9: $(COT^{2-})_2Ce$, |$4f^0L^4$⟩. In the absence of an interaction between Ce and the two COT ligands, states Ψ_1– Ψ_8 have the same energy, and state Ψ_9 is higher in energy by U. Since the model only addresses relative energies, the energy of Ψ_1– Ψ_8 is assigned a value of zero; therefore, the energy of Ψ_9 is U.

In the HMM, the ground state, Ψ_{GS}, is stabilized by interaction (mixing) of Ψ_1–Ψ_8 with the excited state, Ψ_9. Only states in which the Ce electron can "hop" into the COT e_{2u} orbital without changing its spin can interact with Ψ_9. These states are Ψ_1, Ψ_3, Ψ_6, and Ψ_8. The interaction energy is the "hopping integral", t, which is equivalent to the off-diagonal matrix element, H_{12}, in an MO model. Like H_{12}, t reflects the overlap between the ligand and metal orbitals.

The Hamiltonian matrix for the HMM is 9×9; however, the rows and columns for Ψ_2, Ψ_4, Ψ_5, and Ψ_7 contain only zeros. With these states removed, the Hamiltonian is given in eqn (1), where the rows and column correspond to Ψ_1, Ψ_3, Ψ_6, and Ψ_8 and Ψ_9. The Hamiltonian can be solved to evaluate the energy of the ground state, E_{GS}, shown in eqn (2) and its wavefunction, Ψ_{GS}, given by eqn (3). The energy of the MLCT transition, E_{MLCT}, is $\sqrt{U^2+16t^2}$. The values of t and U can be determined from physical measurements of COT_2Ce. From UV-Vis and MCD spectroscopy, E_{MLCT} is 2.63 eV,[16, 45] and from Ce L_3 XANES, N^2 = n_f = 0.89.[13] Using these values, t and U are -0.41 eV and 2.05 eV, respectively, and E_{GS}, the stabilization attributed to 4f-orbital mixing is -0.29 eV (7 kcal mol^{-1}). This value does not include any stabilization resulting from 5d-orbital mixing or electrostatic interactions, which also affect the stability of the complex.

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$$\begin{pmatrix} 0 & 0 & 0 & 0 & -t \\ 0 & 0 & 0 & 0 & -t \\ 0 & 0 & 0 & 0 & -t \\ 0 & 0 & 0 & 0 & -t \\ -t & -t & -t & -t & U \end{pmatrix} \tag{1}$$

$$E_{GS} = \frac{U-\sqrt{U^2+16t^2}}{2} \tag{2}$$

$$\Psi_{GS} = N\left[|4f^1L^3\rangle - \frac{E_{GS}}{2t}|4f^0L^4\rangle\right];\ N^{-2} = 1 + \left(\frac{\Delta E_{GS}}{2t}\right)^2 \tag{3}$$

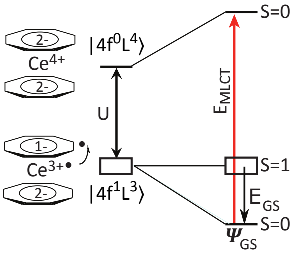

Fig. 1. Bonding in COT_2Ce as described by the HMM. For clarity, the unpaired electron on the COT ligands is shown on a single ligand; it is actually delocalized over both COT ligands.

Temperature Independent Paramagnetism of COT_2Ce

The stabilization of the ground state in COT_2Ce estimated using the HMM can be compared with the stabilization of the singlet state determined from its temperature independent magnetism (TIP). The synthesis of highly pure COT_2Ce by Walter and Andersen enabled its TIP to be accurately measured (χ_{TIP} = 1.4×10^{-4} emu mol^{-1}),[13] which allows an independent estimate of the stabilization of the singlet ground state. The magnitude of the TIP is related to the singlet-triplet gap (E_{GS}) and to the g values of the spins that are coupled in the open-shell singlet ground state.[41] The coupling of the spins may be described using the conventional Heisenberg-Dirac-van Vleck (HDVV) spin Hamiltonian given in eq 4, where 2J is equivalent to E_{GS}.[41] The relationship between 2J and the TIP of the coupled system was determined by Griffith and is shown in eq 5, where N_A is Avogradro's number, μ_B, is the Bohr magneton, g_i is the g-value of Ce(III) in COT_2Ce, and $g_{COT^{\bullet-}}$ is the g-value of $COT^{\bullet-}$, 2.0025.[46]

$$\mathcal{H} = -2J\boldsymbol{S}_{COT^{\bullet-}} \bullet \boldsymbol{S}_{Ce(III)} \tag{4}$$

$$\chi_{TIP} = -\frac{N_A\mu_B^2}{12J}\sum_{i=x,y,z}(g_i - g_{COT^{\bullet-}})^2 \qquad (5)$$

To determine the value of -2J, the values of g_i for Ce(III) are required in addition to χ_{TIP}. For |5/2, 3/2⟩, these are $g_\perp = 0$ and $g_{||} = 2.57$.[47] As previously discussed, the crystal field caused by the COT ligands will mix some |7/2, 3/2⟩ character into the |5/2, 3/2⟩ ground state, which will change the values of $g_\perp$ and $g_{||}$ only slightly. Using the values of $g_\perp$ and $g_{||}$ for |5/2, 3/2⟩, eq 5 yields 2J = -0.32 eV. Since -2J is equivalent to E_{GS}, the stabilization of the singlet state in COT_2Ce determined from its TIP is similar in value to the stabilization of the singlet state in COT_2Ce due to configuration interaction in the HMM model (-0.29 eV). As with the stabilization estimated using the HMM, the stabilization estimated from the TIP does not include the effects based on 5d orbitals or electrostatic interactions.

Discussion

The primary focus of this study was to determine the ground state stabilization in COT_2Ce resulting from 4f orbital mixing. In COT_2Ce, the HMM and analysis of the TIP yield stabilization energies of 0.29 eV and 0.32 eV, respectively. In addition, the stabilization in COT''_2Ce is 0.45 eV (10 kcal mol^{-1}) as determined from the luminescence spectroscopy reported by Amberger, et al.[16] From a practical standpoint, this amount of additional stabilization would greatly enhance separation factors for adjacent lanthanide ions if a complex of only one lanthanide element was stabilized by covalent interactions. While the covalent stabilization in COT_2Ce, 0.3 eV, is substantially larger than in $Cp^*_2Yb(bipy)$,[10] COT^{2-} is not an ideal ligand to enhance orbital mixing with Ce. From the HMM, the value of t in COT_2Ce, -0.41 eV, reflects a relatively strong interaction for a lanthanide complex. In comparison, the value of t in $Cp^*_2Yb(bipy)$ is only -0.16 eV, which is smaller because of the more contracted 4f orbitals of Yb and since only *ca.* 35% of the spin density in $bipy^{\bullet-}$ resides on the N 2p orbitals.[48] On the other hand, the value of U for COT_2Ce, *ca.* 2 eV, is much greater than in $Cp^*_2Yb(bipy)$, 0.4 eV. This large value of U illustrates the paradox noted by Streitwieser and co-workers: COT_2Ce includes both a strong reductant, COT^{2-}, and a strong oxidizer, Ce(IV), when COT_2Ce is described as a formally tetravalent complex.[45] The value of U would decrease if the reduction potential of the ligand was more positive, in other words, if the ligand were less electron rich. However, a less electron rich ligand would likely stabilize Ce(III) less effectively overall, despite the greater covalent contribution relative to ionic stabilization.

While the amount of additional stabilization in COT_2Ce would be sufficient to improve separations, the weak overlap between the 4f orbitals and the ligand orbitals limits the stabilization that can be achieved in lanthanide systems. As a result, the value of t in trivalent lanthanide systems is small, and orbital mixing is largely driven by minimizing U, which results in relatively weak energy degeneracy-driven orbital mixing rather than stronger overlap-driven orbital mixing.[2] While COT^{2-} is not an ideal ligand choice for minimizing U, the value of t in COT_2Ce, 0.41 eV, is probably close to the achievable maximum for trivalent lanthanide coordination complexes since 4f orbitals have their greatest radial extent early in the lanthanide series and all of the carbon 2p orbitals carrying unpaired spin density in $(COT^{1.5-})_2^{3-}$ are directly coordinated to Ce. Using t = 0.41 eV and setting U = 0, the stabilization in the HMM is only -0.8 eV (-19 kcal mol^{-1}), which underscores the limited stabilization achievable in lanthanide complexes by energy degeneracy-driven orbital mixing. This point is also made by Smiles, et al. who suggest that in COT_2Ce, orbital overlap may result in weaker bonding relative to a fully ionic, tetravalent cerium complex (|$4f^0L^4$⟩ ground state) due to a decrease in ionic bonding. While this suggestion appears on the surface to contradict the results shown here that orbital mixing results in a stabilization of *ca.* 0.3 eV, this stabilization is relative to a hypothetical *trivalent* complex. Starting from the perspective of COT_2Ce being a trivalent complex with a |$4f^1L^3$⟩ ground state, 4f-orbital mixing resulting in |$4f^0L^4$⟩ character in the ground state stabilizes the COT_2Ce by *ca.* 0.3 eV. In addition, this interaction stabilizes the complex from an electrostatic perspective as mixing |$4f^0L^4$ ⟩ into the ground state increases the charge on both Ce and the ligands.

The different implications of orbital mixing in COT_2Ce depending on whether one starts from a tetravalent (orbital mixing may destabilize the complex) or trivalent perspective (orbital mixing stabilizes the complex) illustrate an important difference between mixing LMCT states or MLCT states into the ground state in the HMM. In both cases, the stabilization attributed to orbital mixing is the same for given values of t and U. Mixing MLCT character into the ground state increases the charges on both the metal and ligands and should lead to additional stabilization because of electrostatic effects. However, as indicated by Smiles, et al., mixing LMCT character into the ground state decreases the overall electrostatic stabilization of the ground state by decreasing the charges on the metal and ligands. This behaviour may partially explain the difficulty in using orbital mixing to enhance lanthanide separations since orbital mixing involving LMCT may result in little net change in overall stability as a consequence of the opposing effects of electronic and electrostatic stabilization.

Conclusions

The stabilization of the ground state of COT_2Ce due to mixing between the ligand and 4f orbitals was determined to be 0.3 eV using the HMM and from the TIP of COT_2Ce. The previously determined singlet-triplet gap in COT''_2Ce is 0.45 eV.[16] These values are similar to the stabilization determined computationally for COT_2Ce, which vary from 0.33 to 1.1 eV.[31, 34] However, these values do not consider stabilization resulting from to 5d-orbital mixing or electrostatic effects.

This study illustrates the utility of the HMM. In comparison to the more widely employed MO models of bonding, the HMM combines advantages and disadvantages. Its main advantage is that it includes the effect of electron correlation, primarily pairing energy. Other advantages are its simplicity and its close

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relationship to spectroscopy, especially to n_f and E_{MLCT}, which are relatively straightforward to determine. The major disadvantage is that the HMM provides only a limited bonding description compared with a full MO description. It is analogous to a first-order MO model that only includes a single metal orbital and a single set of degenerate ligand orbitals. Moreover, an MO model is often needed to construct the HMM in the first place, which was the case in this study. While Hubbard has shown that it is possible to construct a complete CI model that includes all relevant atomic states analogous to ligand field theory,[40] this is not done in the much simpler HMM.

Overall, HMM and MO models provide analogous descriptions of bonding in COT_2Ce as originally noted by Streitwieser et al.[22] The primary difference between the HMM and MO models is the initial description of the oxidation state in COT_2Ce implied by their basis sets. In the HMM, COT_2Ce is primarily a Ce(III) complex with some Ce(IV) character caused by CI with the MLCT state while in an MO model, COT_2Ce can be described as a Ce(IV) complex with considerable orbital mixing between the Ce 4f and COT π orbitals. In the end, the HMM, MO models, and recent computational models produce analogous descriptions of the ground state, with $n_f \approx 0.9$ regardless of the Ce oxidation state implied by the model.[2, 27-30, 33-35]

Conflicts of interest

There are no conflicts to declare.

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