Calculated Properties of Lanthanocene Anions and the Unusual Electronic Structure of Their Neutral Counterparts

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Selected lanthanocene anions $M(C_8H_8)_2^-$ (M = Ce, Nd, Tb, Yb) and their neutral counterparts have been investigated with large-scale complete-active-space self-consistent field calculations followed by multireference configuration interaction and averaged coupled-pair functional calculations. Relativistic effects were included by means of energy-consistent ab initio pseudopotentials. It is shown that, in contrast to the neutral actinocenes (e.g., M = Th, U), all corresponding lanthanocenes are best described as resulting from trivalent rather than tetravalent central atoms. In addition, the independent-particle model fails to predict the unusual electronic ground states of the Ce, Nd, and Tb systems. The electron affinities of the still hypothetical lanthanocenes beyond the well-known cerocene are found to be almost independent of the central metals and to be substantially higher than those of the corresponding actinocenes. The differences in the electronic structure between lanthanocenes and actinocenes can be explained by the different impacts of relativistic effects, especially on the metal d and f orbitals.

Introduction

Among the organometallic compounds of the lanthanides and actinides, the D_{8h}-symmetric η^8-bound complexes with the ligand cyclooctatetraene, C_8H_8, i.e., bis([8]annulene)metal(IV,-III) or bis(η^8-cyclooctatetraene)metal(IV,III) compounds, were of special interest to both experimentalists[1−4] and theoreticians.[5−8] The bis([8]annulene)metal complexes at the beginning of both rows, i.e., cerocene, $Ce(C_8H_8)_2$ and thorocene, $Th(C_8H_8)_2$, are usually regarded to contain a tetravalent central metal. In a pure ionic picture, a M^{4+} cation with a closed-shell rare-gas electronic configuration (Xe and Rn, respectively) is complexed by two aromatic eight-membered rings $C_8H_8^{2-}$ (10 π electrons per ring). The covalent contributions to the metal−ring bond result from the symmetry-allowed interaction between the 4f/5f and 5d/6d orbitals of the central metal and the π orbitals of the ligands, e.g., in the irreducible representations e_{2u} and e_{2g} of the D_{8h} point group. Due to relativistic effects, the 5f and 6d orbitals of Th are more diffuse than the 4f and 5d orbitals of Ce. Hence, a larger covalent contribution to bonding has been observed for thorocene than for cerocene. The other members of the rows, if they exist in pure or substituted form, are expected to behave rather similarly to cerocene and thorocene, with the exception of the higher complexity of their electronic structure due to a partially filled 4f/5f shell. Details of the chemical bonding in lanthanocenes and actinocenes have been investigated in the framework of density-functional theory by Rösch et al.[6] and by Boerrigter et al.[7] A corresponding discussion of ab initio pseudopotential calculations for cerocene and thorocene was recently published and will not be repeated here.[9]

Despite this appealing simple picture of metal−ring bonding, the stability of a rather ionic compound like cerocene, i.e., of a strong oxidizing agent, Ce^{4+}, together with a strong reducing agent, $C_8H_8^{2-}$, was found to be at least remarkable by Streitwieser et al.[6] The stability of organometallic systems with a tetravalent Ce was frequently discussed thereafter.[2,3] Until recently, cerocene was regarded as one of the very few systems in which such an extreme electronic situation occurs.[4]

The picture of a tetravalent Ce in cerocene was however questioned in 1989 by Neumann and Fulde.[10] On the basis of semiempirical estimates and in analogy to a Kondo ion in a solid, it was argued that Ce should occur as a Ce^{3+} ion with a $4f^1$ occupation. The 4f electron captured by Ce^{4+} is taken from the highest occupied doubly degenerate π orbital of the $C_8H_8^{2-}$ ligands, and the resulting hole is delocalized over both rings. Therefore, on the basis of a one-particle picture and opposite to common belief, cerocene is a compound with a trivalent central metal. This finding would probably not be of greater interest if the 4f electron on Ce and the three π electrons of the

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rings would not couple in the ground state to form a singlet instead of the usually more stable triplet. Note, that experimentally a $4f^1\pi^3$ triplet ground state could be easily distinguished from a $4f^0\pi^4$ singlet ground state, whereas this is not the case for a $4f^1\pi^3$ singlet ground state. At the one-particle level, e.g., in the Hartree−Fock approach, the unusual ground state of cerocene cannot be explained. Specific electron correlations which are not possible for the triplet state, i.e., the configuration interaction between the $4f^1\pi^3$ and $4f^0\pi^4$ configurations, lead to the formation of the singlet ground state with a leading $4f^1\pi^3$ configuration. The term energy of the triplet state was estimated to be only 6 meV mainly due to a large energy gap of 10 eV between the $4f^0\pi^4$ and $4f^1\pi^3$ configurations and the resulting weak configuration interaction.

Quantum chemical ab initio investigations using relativistic energy-consistent ab initio pseudopotentials and various correlation treatments supported the ideas of Neumann and Fulde qualitatively; however, quantitatively the splitting between the $^1A_{1g}$ ground state and the $^3E_{2g}$ excited state (state labels apply for the D_{8h} point group) was calculated to be 1.09 eV.[9] Spin−orbit effects were found to reduce the splitting only by an order of 10%. In addition, theoretically derived data for the photoelectron spectrum, the symmetric metal−ring stretching vibration, and the electronic spectrum agreed with available experimental data for cerocene under the assumption of a $4f^1\pi^3$ $^1A_{1g}$ ground state as well as for thorocene under the assumption of a $5f^0\pi^4$ $^1A_{1g}$ ground state.

Since the overall spatial and spin symmetry $^1A_{1g}$ for the theoretically derived predominantly $4f^1\pi^3$ ground state of cerocene is exactly the same as expected for a $4f^0\pi^4$ configuration (both the singly occupied 4f orbital and the triply occupied π orbital transform according to the e_{2u} irreducible representation in D_{8h}), clear experimental evidence supporting the ideas outlined above was not available. However, recently Edelstein et al. were able to perform XANES (X-ray absorption near-edge structure) spectroscopy for several compounds containing tetravalent and trivalent Ce and found that, for the two substituted cerocenes investigated by them, the signals for the shift of the K-edge with respect to a CeB_6 standard clearly fall in the range for the Ce(III)-containing compounds (0−5 eV).[11] The location of the observed shifts for the cerocenes at 4 eV, i.e., at the side of the spectrum where the compounds with Ce(IV) are found (12−13 eV), is most likely due to the above mentioned configuration interaction between $4f^1\pi^3$ and $4f^0\pi^4$ (contributions 80% and 20%, respectively).[9]

The present work has two goals. First, we want to extend the previous investigations of the ground state of cerocene and the comparison with its heavier homologue thorocene to some other members of the lanthanide and actinide series.[9] Terbocene was selected since terbium (half-filled 4f shell in Tb^{4+}) is, besides cerium (empty 4f shell in Ce^{4+}), the most likely candidate for a tetravalent central atom. Neodymocene was included since its heavier homologue uranocene is the most famous f-element sandwich compound.[12] Finally, ytterbocene was selected because of the position of ytterbium at the end of the lanthanide series. One might anticipate that the 4f hole in a Yb^{3+} central ion behaves analogously to the 4f electron in Ce^{3+}, leading to a $4f^{13}\pi^3$ singlet ground state of ytterbocene.[10] It is clear that ytterbium (filled 4f shell for Yb^{2+}) prefers a divalent rather than a tetravalent situation besides the trivalent case; however, only in the tetravalent case can aromatic closed-shell ligand ring systems be formed. Second, we want to investigate the stability of some lanthanocene and actinocene anions, which has not been done on a theoretical ab initio basis so far. Results of semiempirical calculations on some lanthanide systems were reported 20 years ago, but the emphasis of this work was on magnetic properties and the analysis of metal−ring bonding.[13] In the discussion we will especially focus on the experimental observation that all lanthanocenes except cerocene are yet not known, but their anions $M(C_8H_8)^{2-}$ appear to be quite stable. On the other hand, several actinocenes $M(C_8H_8)_2$ are known, but to our knowledge not the anions for all of them, e.g., for thorocene. We will argue that these characteristic differences can be explained by taking into account the different impacts of relativistic effects in both rows leading to different dominant ground-state configurations for two formally homologous systems and the failure of the independent-particle model to describe the lighter lanthanocenes, i.e., the need to account for electron correlation effects.

Method

The methods applied here are similar to those of previous investigations of cerocene and thorocene and will only be briefly summarized.[9] Scalar-relativistic energy-consistent ab initio pseudopotentials were used to reduce the computational effort by the removal of core electrons and to include the major relativistic effects in an efficient way in the calculations.[14] Small-core pseudopotentials for lanthanides and actinides replacing 28 and 60 core electrons, respectively, were used to avoid any frozen-core errors. For carbon, the $1s^2$ core was replaced by a similar pseudopotential.[14] The corresponding standard valence basis sets applied were (12s11p10d8f)/[4s4p3d2f] for the metals, (4s4p)/[2s2p] for carbon, and (4s1p)/[2s1p] for hydrogen (253 contracted basis functions; basis set A). To check the stability of the results for cerocene and thorocene with respect to an improvement of the basis sets, we also used (12s11p10d8f1g)/[8s7p6d4f1g] for cerium and thorium, (4s4p1d)/[2s2p1d] for carbon, and (4s1p)/[2s1p] for hydrogen (384 contracted basis functions; basis set B). The latter calculations required about 11 GB of disk space for sorting and storing the integrals. A possible symmetry breaking was avoided by state-averaged complete-active-space self-consistent field (CASSCF) calculations covering also nondynamical electron correlation, i.e., possible near degeneracies. The treatment of dynamic electron correlation was performed with the internally contracted multireference configuration interaction including the Siegbahn size-consistency correction (MRCI) and averaged coupled-pair functional (ACPF) methods.[15] Only the energetically highest ligand π orbitals (in order of decreasing energy: e_{2u}, e_{2g}, e_{1u}, and e_{1g}) and the metal f orbitals were treated as active orbitals in the MRCI and ACPF calculations. Although the use of larger active spaces is possible and in fact necessary for very accurate results for cerocene and thorocene,[9] it becomes unfeasible for the systems with a higher f occupation number: using the restricted active space and the small basis set A the largest calculations comprised already up to 2 (107) million contracted (uncontracted) configurations (neodymocene $4f^3\pi^3$).

All calculations were performed with the MOLPRO program system[16] in the D_{2h} point group; however, the D_{8h} symmetry of the metallocenes was maintained throughout. A possible D_{8d} symmetry of the anions[17] as well as their complexation by a counterion or

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embedding in a crystal field was not considered since this would require the use of C_{2v} or an even lower point group in MOLPRO and would result in unfeasibly large computations. In earlier work on $M(C_5H_5)_2$ (M = Eu, Yb),[18] only a very small energy difference of less than 0.01 eV was found between the D_{5h} and D_{5d} geometries. We assume that such a negligible energetic effect would also be found for the systems studied here. An idealized D_{8h} structure of the rings (R(C−C) = 1.392 Å, R(C−H) = 1.090 Å) was used, whereas the metal−ring distance of the neutral systems and their anions was optimized at the CASSCF/ACPF level.[19] Due to the necessary restrictions of the electron correlation treatment, the calculated metal−ring distances are typically too long by about 0.1 Å.[9] We report vertical as well as adiabatic electron affinities; however, the excitation energies of the neutral systems correspond to vertical processes.

It should be emphasized that a well-correlated, fully relativistic treatment of systems of this size is currently unfeasible and simplifications due to pseudopotentials appear to be the best choice. Moreover, the desired high-quality correlation treatment is not possible when the symmetry-lowering spin−orbit interaction is included. Since in previous studies on cerocene spin−orbit coupling was found to be of minor importance,[9] we decided in favor of a good correlation treatment without considering spin−orbit interactions. The basic picture and the major trends resulting from the present investigation will not be altered by inclusion of spin−orbit terms into the Hamiltonian.

In the following discussion, we will denote the relevant metal orbitals as d and f and the energetically highest e_{2u} ligand orbitals as π. The description of configurations in terms of so-called superconfigurations, e.g., $4f^3\pi^3$ for neodymocene, appears to be justified on the basis of the strongly localized character of the singly occupied metal and ligand orbitals. The contributions of individual configurations to the total wave function have been obtained from multiconfiguration self-consistent field (MCSCF) calculations. Since this is not possible at the CASSCF level due to the invariance of the wave function with respect to unitary transformations in the active orbital space, we performed restricted MCSCF calculations with a subset of the configuration space defining the CASSCF wave function; e.g., $4f^3\pi^3$, $4f^2\pi^4$, and $4f^4\pi^2$ were considered for neodymocene, whereas other vanishingly contributing configurations were neglected. On the basis of the corelike character of the metal f orbitals and the predominance of a single configuration in the total wave function of all systems considered here, we think it is justified to describe the electronic structure of the central metal by means of formal oxidation numbers, e.g., Nd(III) and U(IV), and the terms trivalent and tetravalent.

Results and Discussion

The most important results of our calculations on the neutral and anionic lanthanocenes and actinocenes are summarized in Tables 1 and 2, respectively. For a detailed discussion of neutral cerocene and thorocene, including an analysis of metal−ring bonding, the reader is referred to the previous articles.[9] Results of spin−orbit-coupled calculations on uranocene similar to the ones by Chang and Pitzer[8] as well as a detailed study of the excited states of selected neutral lanthanocenes will be published elsewhere.[19] Spin−orbit coupling appears to be of minor importance for the following more chemically oriented discussion[9,19] and was therefore neglected.

Table 1. Selected Properties of Bis([8]annulene)metal Complexes, $M(C_8H_8)_2$, from Scalar-Relativistic Pseudopotential CASSCF/ACPF Calculations (Basis Set B for Ce and Th; Basis Set A Otherwise)[a]

M	$_{58}$Ce	$_{60}$Nd	$_{65}$Tb	$_{70}$Yb	$_{90}$Th	$_{92}$U
at. conf	$4f^15d^16s^2$	$4f^46s^2$	$4f^96s^2$	$4f^{14}6s^2$	$6d^27s^2$	$5f^36d^17s^2$
mol conf	$4f^1\pi^3$	$4f^3\pi^3$	$4f^8\pi^3$	$4f^{13}\pi^3$	$5f^0\pi^4$	$5f^2\pi^4$
GS	$^1A_{1g}$	$^3E_{3g}$	$^6E_{2u}$	$^3B_{2g}$	$^1A_{1g}$	$^3E_{3g}$
d_e (Å)	2.114	2.163	2.036	1.920	2.114	2.047
ω_e (cm^{-1})	178	174	181	207	213	221
ES	$^3E_{2g}$	$^5E_{3g}$	$^8E_{2u}$	$^1A_{2g}$	$^3E_{2u}$	$^1E_{3g}$
T_e (eV)	0.657	0.177	0.112	0.009	2.167	0.693

[a] at. conf = atomic ground-state configuration; mol conf = molecular ground-state configuration; GS = molecular ground state; d_e = metal−ring distance; ω_e = symmetric metal−ring stretching frequency; ES = first excited state with higher or lower spin multiplicity; T_e = adiabatic term energy of ES.

Table 2. Selected Properties of Anionic Bis([8]annulene)metal Complexes, $M(C_8H_8)_2^-$, from Scalar-Relativistic Pseudopotential CASSCF/ACPF Calculations (Basis Set B for Ce and Th; Basis Set A Otherwise)[a]

M	$_{58}$Ce	$_{60}$Nd	$_{65}$Tb	$_{70}$Yb	$_{90}$Th	$_{92}$U
mol conf	$4f^1\pi^4$	$4f^3\pi^4$	$4f^8\pi^4$	$4f^{13}\pi^4$	$6d^1\pi^4$	$5f^3\pi^4$
GS	$^2A_{2u}$	$^4E_{3u}$	$^7A_{2g}$	$^2E_{2u}$	$^2A_{1g}$	$^4E_{3u}$
d_e (Å)	2.180	2.186	2.065	1.955	2.210	2.172
ω_e (cm^{-1})	185	183	185	206	190	187
EA_{ad} (eV)	1.388	2.108	2.167	2.130	−0.032	0.686
EA_{ve} (eV)	1.329	2.101	2.155	2.108	−0.169	0.454

[a] mol conf = molecular ground-state configuration; GS = molecular ground state; d_e = metal−ring distance; ω_e = symmetric metal−ring stretching frequency; $EA_{ad,ve}$ = adiabatic and vertical electron affinities of $M(C_8H_8)_2$.

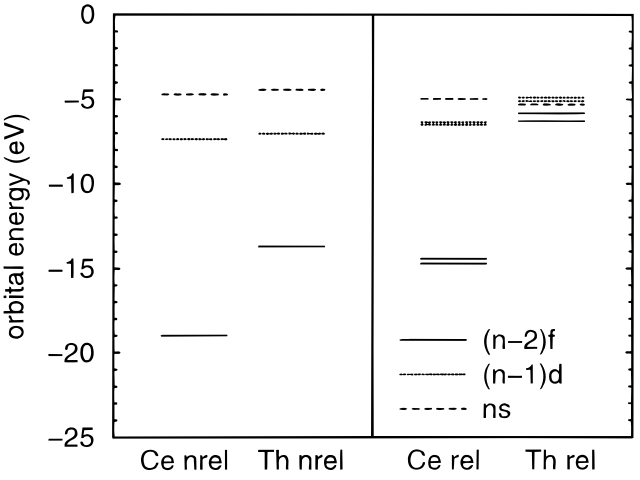

Figure 1. Orbital energies (eV) for the $(n-2)f^1(n-1)d^1ns^2$ configurational average of Ce (n = 6) and Th (n = 7) from nonrelativistic (nrel) Hartree−Fock and relativistic (rel) Dirac−Hartree−Fock calculations.

1. **Atomic Data.** At the beginning of our discussion we want to emphasize the importance of relativistic effects[20] in comparing the lanthanide with the actinide row, especially their impact on the possible valencies of, e.g., Ce and Th. The corresponding atomic data displayed in Figures 1 and 2 have been obtained with the finite-difference multiconfiguration Dirac−Hartree−Fock code GRASP.[21] Whereas both elements appear to be divalent at the nonrelativistic level (Figure 2) [i.e., two of the four valence electrons are in the rather corelike 4f and 5f orbitals (Figure 1)], one and two electrons are promoted from the f shell to the valence d shell for Ce and Th, respectively, due to relativistic effects (Figure 2). The reason is the strong relativistic destabilization of the Ce 4f and especially the Th 5f shell (Figure 1). It already appears from atomic data that Ce is closer to a trivalent than a tetravalent metal, whereas for Th the tetravalent case is clearly preferred.

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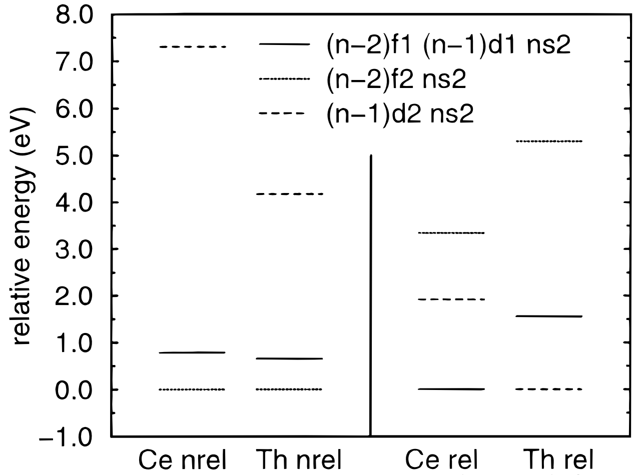

Figure 2. Relative energies (eV) of the $(n-2)f^1(n-1)d^1ns^2$, $(n-2)f^2ns^2$, and $(n-1)d^2ns^2$ configurational averages of Ce ($n = 6$) and Th ($n = 7$) from nonrelativistic (nrel) Hartree–Fock and relativistic (rel) Dirac–Hartree–Fock calculations.

Correlation contributions neglected in these calculations change the picture only qualitatively, not quantitatively. Cerium possesses a $^1G_4$ ground state best to be described by a leading $4f^15d^16s^2$ configuration, whereas the $^3F_2$ ground state of thorium has a predominant $6d^27s^2$ configuration.[22]

2. Cerocene. Considering the atomic results for Ce and Th discussed above, a $5f^0\pi^4$ ground-state configuration of thorocene is expected, but the leading $4f^1\pi^3$ configuration in the ground state of cerocene[9−11] also should not come as a too big surprise. Moreover, it is clear from the orbital energies displayed in Figure 1 (Ce $4f_{5/2}$ −14.73 eV, $4f_{7/2}$ −14.45 eV; Th $5f_{5/2}$ −6.28 eV, $5f_{7/2}$ −5.82 eV) that it is unlikely to detect a 4f peak in the low-energy region (5−7 eV) of the photoelectron spectrum of cerocene. The 4f peak will occur at an energy above 10 eV and will be hidden by the broad structures resulting from the ionization of the ligand orbitals. In contrast to this, the missing 5f peak for thorocene ($5f^0\pi^4$) and its presence at 6.2 eV for uranocene ($5f^2\pi^4$) can indeed be used to test the occupancy of the 5f shell.[23]

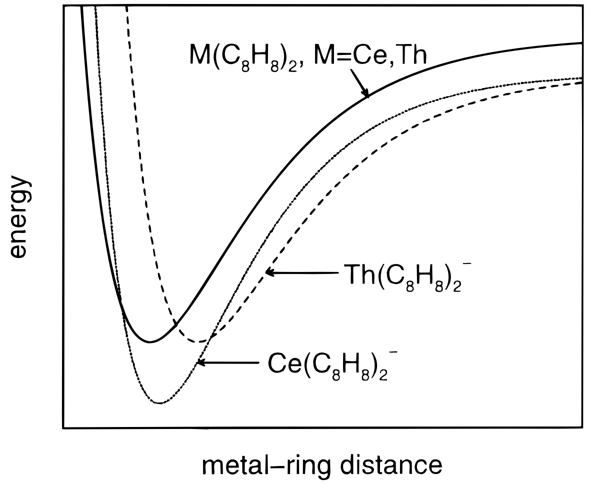

Figure 3. Schematic plot of the potential curves of $Ce(C_8H_8)_2$ and $Th(C_8H_8)_2$ (solid line; the same curve was assumed for simplicity) and their anions $Ce(C_8H_8)_2^-$ (dotted line) and $Th(C_8H_8)_2^-$ (dashed line). The energy difference between the neutral and ionic systems at large metal−ring distance corresponds to the electron affinity of cyclooctatetraene, C_8H_8.

Using a purely ionic picture, the anions of the lanthanocenes and actinocenes have the charge distribution $M^{3+}(C_8H_8^{2-})_2$. The electron configuration of the $Ce(C_8H_8)_2^-$ anion is $4f^1\pi^4$. The singly occupied 4f orbital belongs to the a_{2u} irreducible representation of the D_{8h} point group. The vertical electron affinity of cerocene at the theoretical metal−ring equilibrium distance has been determined to be 1.59 eV (basis set A; basis set B yields 1.33 eV) at both the MRCI and ACPF levels. The dependency of the vertical electron affinity EA (eV) on the metal−ring distance d (Å) near the equilibrium distance may be expressed with an accuracy better than 0.01 eV by a second-order polynomial, i.e., $EA = c_0 + c_1d + c_2d^2$ (c_0, c_1, c_2: basis set A −9.7943, 9.3479, −1.8920; basis set B −16.2581, 14.7623, −3.0479). Due to this strong distance dependency, it is very important to distinguish whether calculated or experimental metal−ring distances are used. For a given basis set, the adiabatic values (basis set A 1.61 eV; basis set B 1.39 eV) are very similar to the vertical ones, indicating that only a small geometry relaxation takes place upon addition of an electron. According to our results, the very low redox potential of −1.28 eV reported by Streitwieser et al.[6] for the bis([8]annulene)-cerium(IV)/cerate(III) couple and the ease with which the anion can be chemically converted to the neutral system by using mild oxidizing agents like silver iodide is due to the removal of an electron from the ligand π orbitals rather than from the 4f shell. The lowering of the energy of the neutral system due to the strong configuration interaction between $4f^1\pi^3$ and $4f^0\pi^4$ [9] further reduces the ionization potential of the anion.

In contrast to the case of cerocene, we did not find a positive value for the vertical electron affinity of thorocene. The free anion is nevertheless metastable at a larger metal−ring distance. The adiabatic electron affinity of thorocene at the ACPF level is −0.07 eV (basis set A; basis set B yields −0.03 eV; the vertical values are −0.21 and −0.17 eV for basis sets A and B, respectively). The additional electron is in an a_{1g} orbital, which has contributions of roughly 76% and 22% from Th 6d and 7s, respectively. Whereas for cerocene the central cerium stays in oxidation state III upon going from the neutral system to the anion and the metal−ring distance is only slightly increased, the thorium in thorocene goes from oxidation state IV in the neutral system to III in the anion and the resulting metal−ring distance increase is much larger. The situation is schematically depicted in Figure 3. We predict salts with $Th(C_8H_8)_2^-$ anions to be quite unstable compared to those containing cerium or uranium (cf. below), although it might be possible to stabilize them by large cations with very low electron affinities.

The reason for the differences between cerocene and thorocene appears to be the relativistic destabilization of the Th 5f valence orbitals. Note that both Ce^{3+} and Th^{3+} have an $f^1\ ^2F_{5/2}$ ground state.[22] The ionization potential of Th^{3+} (28.65 eV) is, however, considerably lower than that of Ce^{3+} (36.76 eV) due to the increased relativistic effects; i.e., free Th^{4+} an additional electron less readily accepts than free Ce^{4+}. The Th 5f and 6d orbitals are significantly involved in metal−ring bonding; however, the 5f orbitals are more compact than the 6d orbitals. Their explicit occupation in the anion leads to a larger electron−

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electron repulsion and is therefore less favorable than the occupation of a 6d−7s hybrid orbital.

If the picture for cerocene and thorocene is extended to the other members of both series, one expects $4f^n\pi^3$ and $5f^{n-1}\pi^4$ (n = 1−14 for Ce to Lu and for Th to Lr) configurations for lanthanocenes and actinocenes, respectively. However, configuration interaction between $4f^n\pi^3$ and $4f^{n-1}\pi^4$ might lead to lanthanocenes with spatial and spin symmetry of the ground states indistinguishable from those obtained for the corresponding actinocenes. The ground states of the anions are expected to result from $4f^n\pi^4$ configurations for lanthanocenes and $5f^{n-1}6d^1\pi^4$ or $5f^n\pi^4$ configurations for actinocenes.

Finally, the question of the choice of the basis set has to be addressed. Due to the open f shell of the heavier lanthanocenes and actinocenes, the use of the larger basis set B would lead to unmanageable long CI expansions for these systems (cf. above). In case of cerocene (thorocene), we derived for basis sets A and B, respectively, values for the metal−ring distance of 2.181 (2.136) Å and 2.114 (2.114) Å and for the symmetric metal−ring vibrational frequency of 178 (211) cm^{-1} and 179 (213) cm^{-1}. As discussed above, the values of the vertical and adiabatic electron affinities obtained with both basis sets agree within 0.27 (0.04) eV. For the anion, the corresponding results were 2.222 (2.230) Å and 2.180 (2.210) Å for the metal−ring distance as well as 182 (189) cm^{-1} and 185 (190) cm^{-1} for the symmetric metal−ring vibrational frequency. On the basis of these results, we think that the use of the smaller basis set A is justified for the investigation of the heavier lanthanocenes and actinocenes.

3. Neodymocene. Uranocene, $U(C_8H_8)_2$, was first synthesized by Streitwieser and Müller-Westerhoff in 1968[12] and is the theoretically most extensively investigated bis([8]annulene)-metal complex.[6−8] Undoubtedly it has to be regarded as a U(IV) compound.[19] In a simple ionic picture, the U^{4+} ion with a $5f^2$ configuration is sandwiched by two aromatic $C_8H_8^{2-}$ rings. At the multiconfiguration self-consistent field level, the $5f^2\pi^4$ configuration contributes to the $^3E_{2g}$ ground state with 93%; the admixtures of $5f^3\pi^3$ and $5f^4\pi^2$ are about 4% and 3%, respectively. The comparison to the lighter homologue neodymocene, $Nd(C_8H_8)_2$, is interesting: as expected from the discussion above, it is clearly a Nd(III) compound with a predominant $4f^3\pi^3$ configuration yielding a contribution of 97%. Small admixtures result from the $4f^2\pi^4$ and $4f^4\pi^2$ configurations and lead to a $^3E_{2g}$ ground state as in case of uranocene. Note, however, that the $^3E_{2g}$ ground state for uranocene can be explained by an effective one-particle picture, e.g., using a single electronic configuration, whereas this is not the case for neodymocene: including only the $4f^3\pi^3$ configuration, a $^5E_{2g}$ ground state is obtained! Figure 4 shows the density of states for the low-lying triplet and quintet states without and with configuration interaction. The horizontal arrows show the energetic shift of the $^3E_{3g}$ ground state and the $^3E_{2g}$ first excited state due to the correlation effects, i.e., an obvious breakdown of the independent-particle picture. The triplet−quintet splitting of 0.18 eV is considerably lower than the corresponding singlet−triplet splitting found for cerocene (0.33 and 0.66 eV for basis sets A and B, respectively; 1.09 eV was found previously for a valence double-ζ basis set in connection with a much larger active space[9]). The reason appears to be the increasing core character of the 4f shell upon going from left to right in the lanthanide series and the corresponding weakening of the configuration interaction mechanism.

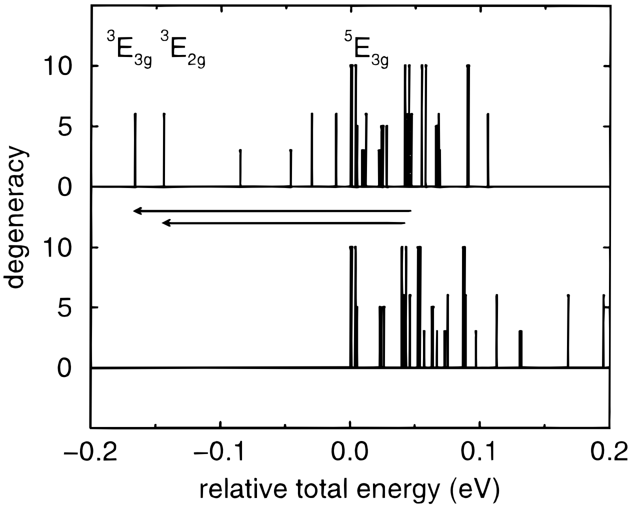

Figure 4. Density of states for neodymocene $Nd(C_8H_8)_2$ from MCSCF calculations for states of the leading $4f^3\pi^3$ configuration without (below) and with (above) admixture of the configurations $4f^2\pi^4$ and $4f^4\pi^2$. The lowest quintet state, $^5E_{3g}$, is used to mark the origin of the energy axis. The lowest triplet state, $^3E_{3g}$, is located at −0.17 eV. The arrows indicate the energetic shifts of the two lowest triplet states due to configuration interaction.

The vertical electron affinity of neodymocene at the MRCI and ACPF levels was determined to be 2.10 eV. This value is 0.51 eV higher (basis set A; basis set B yields 0.77 eV) than the one for cerocene and very similar to the ones obtained for the other members of the 4f row investigated here, i.e., 2.16 eV for terbocene and 2.14 eV for ytterbocene. A straightforward explanation is as follows: considering $M^{3+}(C_8H_8^{1.5-})_2 + e \rightarrow M^{3+}(C_8H_8^{2-})_2$ as a simple model, the additional electron goes into the e_{2u} ligand orbital and the electron affinity should be rather independent of the central metal. However, in cases where a strong configuration interaction between $M^{3+}(C_8H_8^{1.5-})_2$ and $M^{4+}(C_8H_8^{2-})_2$ is present, i.e., for cerocene, the energy of the neutral lanthanocene is significantly lowered and a reduced electron affinity results. Note that the sum of the adiabatic excitation energies in Table 1, which provide a measure for the importance of configuration interaction in the neutral system, and the adiabatic electron affinities in Table 2 is rather constant along the lanthanide series (Ce 1.94 eV (basis set A; basis set B yields 2.05 eV); Nd 2.29 eV; Tb 2.28 eV; Yb 2.12 eV) and supports this simple model. The adiabatic electron affinity of neodymocene is only 0.01 eV higher than the vertical value, and the metal−ring distance becomes less than 0.03 Å larger upon electron capture, which is obviously only a small perturbation. The synthesis of lanthanocenes other than cerocene also should be feasible by oxidation of their anions; however, stronger oxidizing agents have to be used than in the case of cerocene.

The vertical electron affinity of uranocene is small (MRCI 0.34 eV; ACPF 0.45 eV) but, in contrast to that of thorocene, positive. We attribute this to the stabilization of the 5f shell due to incomplete shielding of the nuclear charge upon going from left to right in the actinide series. In other words, the stabilization due to shell structure effects overcompensates the destabilization due to dominating indirect relativistic effects (cf., e.g., the atomic data tables and plots published by Desclaux[27]). Since the additional electron goes into a metal 5f orbital, we expect the electron affinities of the actinocenes to be metal-dependent and to increase from left to right. The adiabatic electron affinity of uranocene is 0.23 eV larger than the vertical value, and the metal−ring distance increases from the neutral

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system to the anion by 0.12 Å. The latter value is close to the difference of the crystal radii of U^{3+} and U^{4+} (coordination number 6) of 0.14 Å;[28] i.e., uranocene is a uranium(IV) compound and its anion a uranium(III) compound.

4. Terbocene. Besides cerocene, $Ce(C_8H_8)_2$, it is terbocene, $Tb(C_8H_8)_2$, which might be a possible candidate for an organometallic lanthanide compound with a tetravalent metal. This suggestion is mainly motivated by the special stability of a half-filled 4f shell on Tb. However, in the present calculation, clearly a Tb(III) compound with a leading $4f^8\pi^3$ configuration contributing about 89% to the $^6E_{2u}$ ground state is found. The $4f^7\pi^4$ and $4f^9\pi^2$ configurations contribute with about 7% and 4%, respectively, and cause a sextet−octet splitting of 0.11 eV. We note that the overall symmetry and multiplicity of the ground state is the not same as one would expect for the $4f^7\pi^4$ configuration of a Tb(IV) compound! If it would be possible to synthesize terbocene, the experimental proof of our model should be easier, e.g., by means of electron spin resonance, than in case of cerocene.

The vertical and adiabatic electron affinities of terbocene are almost identical, i.e., 2.16 and 2.17 eV, and the metal−ring distance increases only by 0.03 Å upon going from the neutral system to the anion.

5. Ytterbocene. At the end of the lanthanide series, ytterbocene, $Yb(C_8H_8)_2$, is also a compound with a trivalent central metal, but due to the large energetic separation of the almost exclusively contributing $4f^{13}\pi^3$ configuration from the $4f^{12}\pi^4$ and $4f^{14}\pi^2$ configurations, their interaction is rather weak and the singlet state does not fall below the triplet state anymore. Due to the corelike character of the 4f shell and the small interaction with the open-shell ligand orbitals, the singlet−triplet splitting is found to be very small, i.e., 0.01 eV.

Similar to those of terbocene, the vertical and adiabatic electron affinities of ytterbocene are rather similar (2.11 and 2.13 eV) and the increase in the metal−ring distance is less than 0.03 Å. Besides the $Yb(C_8H_8)_2^-$ anion, the $Yb(C_8H_8)_2^{2-}$ dianion is also known.[24] We did not find a positive value for the electron affinity of $Yb(C_8H_8)_2^-$ at metal−ring distances below 5 Å. Of course, since C_8H_8 has a positive electron affinity (ACPF values for correlating only the π HOMO: 0.33 eV for basis set A; 0.43 eV for basis set B), the energy of $Yb(C_8H_8)_2^{2-}$ falls below that of $Yb(C_8H_8)_2^-$ at large distances. In order to exist as a chemically bound anion, however, $Yb(C_8H_8)_2^{2-}$ has to be stabilized by a countercation.

Finally, the difference between the metal−ring distances of the Yb and Ce systems can be used in order to obtain an estimate of the lanthanide contraction. Values of 0.194 and 0.224 Å are calculated for the neutral systems and anions, respectively. These values are at the upper limit of what has been obtained for other systems; e.g., values of 0.19, 0.06, and 0.12 Å were obtained in quasirelativistic density-functional calculations for the diatomic lanthanide hydrides, oxides, and fluorides, respectively,[25] while correlated pseudopotential calculations yielded values of 0.09, 0.06, and 0.10 Å.[26] A large lanthanide contraction is a result of a weak bond[25] and indicates a relatively small participation of the 4f orbitals in chemical bonding; cf., e.g., the discussion by Dolg and Stoll.[5] The experimentally derived ionic radii of La^{3+} and Lu^{3+} (coordination number 6) yield a value of 0.17 Å,[28] indicating that the situation of the lanthanides in lanthanocenes indeed corresponds to a Ln^{3+} ion complexed by two $C_8H_8^{1.5-}$ rings.

Conclusions

Large-scale ab initio calculations including the most important relativistic effects show that the ground-state electron configuration of the lanthanocenes is best described as arising from a trivalent central metal ($f^n\pi^3$) rather than a tetravalent central metal ($f^{n-1}\pi^4$) which is found for the actinocenes. The corresponding anions have a trivalent central metal ($d^1\pi^n$ for thorocene; $f^n\pi^4$ otherwise) for both rows. Formally the lanthanocenes are related to the corresponding actinocenes by the dropping of one electron from the highest occupied ligand π orbital into a metal f orbital. The reason for the differences between the two rows has been traced to relativistic effects, i.e., the larger destabilization of the metal d and f valence orbitals for the actinides. For the early lanthanocenes neodymocene and terbocene, it was found in agreement with previous work on cerocene that the independent-particle picture breaks down and a multiconfiguration description is necessary in order to explain the spin and spatial symmetries of the ground states. We suggest that the difficulties in synthesizing lanthanocenes, except cerocene, as well as the ease with which the corresponding anions are obtained are due to the unusual electronic structure reported here. The hole in the chemically easily accessible ligand π orbital makes the compounds reactive and is also responsible for their almost metal-independent electron affinity, again with the exception of cerocene. The rather low value in the latter case and the ease with which, e.g., $K^+[Ce(C_8H_8)_2]^-$ can be electrochemically converted to cerocene are mainly due to strong configuration interaction in the ground state of the neutral system and the corresponding stabilization. The anion of thorocene appears to be the least stable member of the actinocene series, mainly due to relativistic effects. Since shell-structure effects become more important upon going from left to right in the series, we predict an increasing stability of the anions formed by uranocene and the heavier actinocenes.

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