



Two interpretations of the cerocene electronic ground state



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ABSTRACT

Two alternative interpretations are given for the electronic ground state of bis- η^8 -annulene[8] cerium, cerocene, based on the same relativistic Douglas–Kroll–Hess complete active space all-electron wavefunction. Rotations in the spaces of the one- and many-electron wavefunctions, leaving the total energy invariant, show that the system can be viewed as a complex of a closed-shell Ce(IV) ion sandwiched by two aromatic annulene[8] dianions and bonded with a significant Ce 4f – ring π covalency, or as a Ce(III) ion with an almost atomic-like 4f¹ subconfiguration, coupled to the unpaired electron in the rings highest energy occupied π orbitals in a Kondo-type fashion.

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1. Introduction

Cerocene, bis- η^8 -annulene[8] cerium Ce (C₈H₈)₂, was first synthesized by Greco et al. in 1976 [1] as a lanthanide analogue to the famous D_{8h}-symmetric actinide sandwich compound uranocene U (C₈H₈)₂ discovered earlier by Streitwieser and Müller-Westerhoff [2], however, more than three decades later the electronic structure of cerocene is still under a vivid debate [3–14]. In 1983 Rösch and Streitwieser reported that quasirelativistic self-consistent field scattered-wave calculations yielded an unexpected similarity of the electronic structure of cerocene to that of thorocene (bis- η^8 -annulene[8] thorium (IV)) and uranocene (bis- η^8 -annulene[8] uranium (IV)), e.g. a f electron count as high as 1.62 as well as an unusual and unprecedented involvement of the Ce 4f orbitals in metal–ring bonding [15]. Streitwieser and coworkers pointed out that already the existence of cerocene should be considered to be remarkable, since the complex combines the strong oxidizing agent Ce⁴⁺ with two [8]annulene dianion rings C₈H₈²⁻, which are strong reducing agents [3]. The similarity of the photoelectron spectra of cerocene and thorocene, especially the absence of a low-energy peak arising from a partially occupied f shell as observed e.g. in uranocene, lead to the assignment as a bis- η^8 -annulene[8] cerium (IV) compound.

A new view of the electronic structure of cerocene was initiated by Fulde and Neumann in 1989 [4]. Inspired by 4f and 5f Kondo lattice systems exhibiting spectacular low-temperature phenomena the authors conjectured that in its ground state cerocene might be a molecular Kondo analogue, i.e. a Ce³⁺ ion is complexed by two C₈H₈^{1.5-} rings and the unpaired electrons in the metal 4f and ligand π orbitals are coupled to form an open-shell singlet. Their view was

confirmed by Dolg et al. in 1991 by large-scale multi-configuration self-consistent field (MCSCF) calculations including relativistic effects by means of a Ce pseudopotential (PP), which yielded contributions of 82.8% 4f_{e2u}¹ π _{e2u}³ and 17.2% 4f_{e2u}⁰ π _{e2u}⁴ for the ¹A_{1g} ground state [5]. In 1995 MCSCF, multi-reference configuration interaction (MRCI) and multireference averaged coupled-pair functional (MRACPF) calculations, also corrected for spin–orbit interaction, provided first *ab initio* results for the electronic spectrum, the metal–ring distance and the symmetric metal–ring vibration of cerocene and thorocene [6]. Using a Mulliken population analysis a f electron count of 1.08 was derived for the cerocene ground state. Aside from supporting the previous findings it was argued that due to the low energy of the Ce 4f shell a peak in the photoelectron spectrum of cerocene arising from a Ce 4f¹ occupation has to show up at higher energies than those for the ligand π _{e2u} (\approx 6.75 eV) and π _{e2g} (\approx 7.68 eV) orbitals, whereas due to the strong relativistic destabilization of the U 5f shell the peak arising from U 5f² (\approx 6.15 eV) is located at lower energies than those for the uranocene π _{e2u} (\approx 6.80 eV) and π _{e2g} (\approx 7.75 eV) orbitals. Thus, whereas the absence of a low-energy f peak in the photoelectron spectra supports a bis- η^8 -annulene[8] thorium (IV) complex, this is not the case for cerocene, which rather should be viewed as a bis- η^8 -annulene[8] cerium (III) compound [6].

In 1996 Edelstein and coworkers published X-ray absorption near-edge structure (XANES) studies, using the Ce L- and K-edges to determine the oxidation state [7]. It was found that two substituted cerocene systems yielded spectra closer to typical Ce(III) compounds than to Ce(IV) compounds, thus confirming the theoretical studies. Amberger and coworkers concluded from low-temperature absorption and luminescence spectra as well as magnetic circular dichroism (MCD) measurements that cerocene is more likely a cerium (III) compound [8]. Further evidence for a molecular Kondo effect in cerocene was gained by Booth et al. with magnetic measurements and XANES studies [9], leading to a f electron count

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of 0.89 ± 0.03 . Finally, in 2009 Walter et al. published besides new synthetic procedures for the preparation also extensive experimental studies, i.e. magnetic measurements, extended X-ray absorption fine structure (EXAFS) and XANES spectroscopy, on unsubstituted cerocene confirming the admixture of the $4f_{e_{2u}}^1 \pi_{e_{2u}}^3$ and $4f_{e_{2u}}^0 \pi_{e_{2u}}^4$ configurations in the ground state, with the first configuration most likely dominating [10].

The assumption of a Kondo-type ground state of cerocene however was not uniquely accepted. Streitwieser et al. published in 2004 chemical evidence that cerocene behaves remarkably like bis- η^8 -annulene[8] actinide (IV) compounds [11]. A combined experimental and quantum chemical study of related bis- η^8 -pentalene cerium complexes lead Balazs et al. in 2007 to recommend a classification of these and cerocene as Ce(IV) systems [12]. Kerridge et al. reported in 2009 results of all-electron (AE) complete active space second-order perturbation theory (CASPT2) calculations using the second-order scalar-relativistic Douglas–Kroll–Hess Hamiltonian (DKH2) [13]. In contrast to the previous *ab initio* MRCI and MRACPF studies they found an excellent agreement for the calculated metal–ring distance (1.964 Å) with the experimental value (1.969 Å [16]), emphasizing the accuracy of their approach. Their work yields a f electron count of 0.90 ± 0.04 , exhibiting only a slight dependency on details of the calculation. According to their analysis of a two-state (ground and first excited state) averaged calculation 58.1% of the ground state wavefunction have $4f^0$, only 23.4% $4f^1$ and 8.7% $4f^2$ character. Thus, in line with Streitwieser et al. the authors state that cerocene is best described as a Ce(IV) system in which a transfer of electron density from the rings to the metal leads to an effective oxidation state lower than the formal value of +4, which might in certain cases even be closer to +3. The authors further argue that the concept of a formal oxidation state is not well defined for a multiconfigurational ground state as that of cerocene, and they rather recommend to analyze the wavefunction in terms of natural orbital occupancies. Based on the distinction that a Ce(III) compound would be expected to have a metal-localized singly occupied f orbital, whereas Ce(IV) would have not, cerocene better fits into the latter category, despite its significant f density. This view is supported by a recent article of Kerridge reporting an analysis of the CASSCF wavefunction [14].

The current contribution aims to show that these two different interpretations of the cerocene ground state are in fact related by a unitary transformation of the Ce 4f and ligand π orbitals in e_{2u} symmetry of the D_{8h} point group, when a CASSCF wavefunction (as a leading contribution to higher correlated CASPT2, MRCI or MRACPF wavefunctions) is used to describe the $^1A_{1g}$ ground state. Although this explanation is relatively trivial, it was so far not given in the literature. Additional results using also larger basis sets and including higher electron correlation contributions will be published elsewhere.

2. Method

The calculations reported here have been carried out at the AE level using the DKH2 Hamiltonian. H and C were described by DKH2-adapted augmented correlation-consistent basis sets of valence triple-zeta quality (aug-cc-VTZ) containing up to p and d functions for H and C, respectively [17,18]. For Ce a segmented contracted DKH2-optimized (23s16p12d6f3g)/[18s12p9d3f3g] basis set was used [19]. In order to distinguish in the wavefunction analysis e.g. between Mulliken 4f and f populations an atomic natural orbital (ANO) generalized contraction to a (23s16p12d6f3g)/[9s8p6d4f3g] basis set was also applied. The Ce 4f orbitals as well as the highest occupied ligand π orbitals were included in the active space. All calculations were carried out with the MOLPRO quantum chemistry program package [20] in D_{2h} symmetry, however D_{8h} was maintained for the molecule. An optimized geometry

with a Ce–ring distance of 1.971 Å, as well as C–C and C–H bond distances of 1.410 Å and 1.074 Å, respectively, was used unless otherwise noted. The C–H bonds are tilted by about 5.6° out of the C_8 plane towards the Ce center. This geometry is close to the one obtained by Kerridge et al. [13], who only optimized the metal–ring distance (1.964 Å) and assumed the rings to be planar with fixed C–C (1.404 Å) and C–H (1.087 Å) bond distances. It should be noted that so far only *ab initio* methods with a perturbative treatment of dynamical correlation effects, i.e. CASPT2 and CASSCF/RS2, were able to yield a metal–ring distance in close agreement with the experimental value, whereas previous MRCI and MRACPF calculations yielded values about 0.08 Å too long [6].

The CASSCF natural orbitals in the active space correspond to (mixtures of) 4f and π in the doubly degenerate e_{2u} irreducible representation of the D_{8h} molecular point group and are denoted hereafter as orbitals a' and b' . These orbitals were rotated according to $a = a' \cos \alpha + b' \sin \alpha$ and $b = b' \cos \alpha - a' \sin \alpha$ with rotation angles α between -20° and $+70^\circ$, in steps of 2.5° , leaving the total energy invariant. The f character of the active orbitals was determined by a Mulliken population analysis. The boundaries for the rotation angle stated above correspond to the points where both active orbitals in each of the a_u and b_{1u} irreducible representations of D_{2h} have an identical f contribution of about 50%. The CI coefficients for each rotation angle were determined by applying the full-CI code in MOLPRO [20] and the corresponding contributions of the configurations were calculated. Although this procedure is quite costly, it circumvents the transformation to natural orbitals which is usually done and prohibits an analysis in terms of configurations built from orbitals with well-defined metal 4f and ligand π character. Excitations outside of the CASSCF space were not considered since these cannot be associated with configurations in which only valence orbitals are occupied and which are thus useful for a chemists view of electronic structure. Moreover, at the CASSCF/MRCI level the higher natural orbitals have only quite small occupations indicating that the leading CASSCF wavefunction describes most of the physics. Note that although the orbital rotation has a 90° period, the CI coefficients of a specific configuration $a^n b^{4-n}$ exhibit a 180° period for $n = 0, 1, 3, 4$ and a 90° period for $n = 2$. The curves for $n = 0$ and $n = 4$ as well as for $n = 1$ and $n = 3$ are shifted by 90° , since a and b change their character with a 90° period.

3. Results and discussion

The main results of the present Letter are given in Figure 1. The upper plot shows the f character of an active orbital pair in the a_u or b_{1u} irreducible representation of the D_{2h} point group used in the calculations, corresponding to one component of each of the two active orbitals pairs in the e_{2u} irreducible representation of the actual molecular point group D_{8h} . The natural orbitals derived at the CASSCF level correspond to an angle of 0° and exhibit a significant mixing, i.e. orbital a' is mainly a ligand π orbital ($\approx 80\%$) with significant admixture of 4f ($\approx 20\%$), whereas orbital b' is essentially complementary with a high 4f contribution ($\approx 80\%$) and a smaller ligand π orbital admixture ($\approx 20\%$). The lower plot provides the corresponding configuration contributions. It is seen that for the CASSCF natural orbitals the a^4 closed-shell configuration dominates, with smaller contributions of $a^2 b^2$ and $a^3 b^1$. A maximum contribution of the a^4 configuration ($\approx 81\%$) is obtained by rotating with an angle of about -4.5° , leading to a slightly stronger orbital mixing. This situation, which is denoted by the left vertical line in Figure 1, corresponds essentially to what is referred to in the literature as a Ce(IV) system with significant metal–ring covalency, as described by Streitwieser and coworkers [3,11].

Rotation of the a' and b' natural CASSCF orbitals by about 25° leads to a minimum f character (less than 5%) in the a orbital,

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