C. R. Chimie 13 (2010) 853–859

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

All-electron CASPT2 study of Ce(η^8–C_8H_6)$_2$

Andrew Kerridge, Nikolas Kaltsoyannis *

Department of Chemistry, University College London, 20, Gordon Street, London WC1H 0AJ, UK

ARTICLE INFO

Article history:
Received 10 November 2009
Accepted after revision 9 February 2010
Available online 24 March 2010

Keywords:
Electronic structure
Cerium
Computer chemistry
Ab initio calculations
Density functional calculations
Metallocenes
Lanthanides

ABSTRACT

CASSCF wave functions and CASPT2 energies are presented for the ground and 15 and 31 excited states of the D_{2d} and D_{2h} conformers respectively of the f-element sandwich molecule $CePn_2$ (Pn = η^8–C_8H_6). The ground states of both conformers are found to be strongly multiconfigurational, analogous to cerocene, $CeCOT_2$ (COT = η^8–C_8H_8), as reported in *Journal of Physical Chemistry A* **113** (2009) 2896. Investigation of the nature of the multiconfigurational character shows that the analogy with cerocene is indeed strong. It is shown that the occupations of the natural orbitals produce a more reliable description of the $CePn_2$ ground state than does the configurational admixture, and that these occupations can be used to deduce a value for the total f-density in the system. This density is found to be slightly lower than that of cerocene, and is in good agreement with that found experimentally. A density functional theory calculation of the same system is able to broadly capture the important features of the electronic structure, but is unable to replicate the experimental value of the total f-density. CASPT2 calculations reproduce the energy of the first band in the UV/Vis spectrum of $CePn^*_2$ (Pn* = η^8–C_8Me_6) to within 0.01 eV. Although this extremely good agreement is probably somewhat fortuitous, it highlights the fact that multiconfigurational methods are required in order to model systems such as $CePn_2$ to a high level of accuracy.

1. Introduction

The f-element metallocenes M(η^8–C_8H_8)$_2$ (M = Ln, An) have received considerable attention, both experimental and theoretical, since the original synthesis of uranocene, $UCOT_2$ (COT = C_8H_8), in 1968 by Streitwieser and Müller-Westerhof [1]. Subsequently, Th, (substituted) Pa, Np and Pu analogues of uranocene have been synthesized [2–4], along with the lanthanide analogue, cerocene, $CeCOT_2$ [5,6]. Compounds incorporating the other example of an aromatic eight-membered ring system, pentalene (Pn = C_8H_6), have, however, received comparatively little attention, "in part due to synthetic difficulties" [7]. Compounds with substituted pentalene ligands have been reported for Th and U [7,8] and Ce [9,10], but computational investigations have not been performed to the same theoretical level as for the COT-containing systems. This is of particular importance for the cerium compounds, for whilst there is little doubt that the actinocenes synthesized to date contain a tetravalent actinide ion, opinion with regard to cerocene is divided. We have discussed this is in detail in recent publications [11,12], and so only briefly summarise here.

Streitwieser et al. [6] and Raymond et al. [13,14] have argued strongly for a +4 oxidation state in cerocene. This interpretation, however, implies the presence of two highly reducing COT^{2-} rings in close proximity to the strongly oxidizing Ce^{4+} cation. An alternative to this (somewhat unlikely) formulation was proposed by Neumann and Fulde [15] and supported by sophisticated *ab initio* calculations on cerocene and the actinide analogue [16–19] by Dolg et al. They concluded that the ground states of both systems is $^1A_{1g}$, and that thorocene is clearly a Th(IV) compound. Cerocene, however, exhibits strong

---

* Corresponding author.
E-mail address: n.kaltsoyannis@ucl.ac.uk (N. Kaltsoyannis).

1631-0748/$ – see front matter © 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2010.02.006

multiconfigurational character, with the dominant (c. 80%) configuration involving the occupation of a single metal-localised valence $4f_\delta$ level, with a corresponding hole in the highest occupied ring-based π orbitals of e_{2u} symmetry. Thus $CeCOT_2$ is best described as a Ce(III) compound containing two COT rings each carrying a formal 1.5– charge. This view has received (strong) experimental support via XANES measurements [20,21], and optical spectroscopic properties of substituted cerocenes have been shown to be more consistent with a bonding model based on Ce(III) than Ce(IV) [22].

Recent attention has turned to the pentalene (Pn, η^8–C_8H_6) analogue of $CeCOT_2$. Balazs et al., after detailed spectroscopic, magnetic and density functional theory (DFT) [23,24] studies, conclude that for $CePn_2$, "a classification of a formal oxidation state IV is recommended" [9]. Interestingly, some of the same authors have also studied the permethylated analogue, $CePn^*{}_2$ ($Pn^* = \eta^8$–C_8Me_6) using similar methodology, and concluded that "the [XANES spectroscopy] gives strong evidence for a formal valency close to Ce(III) in this molecule" [10]. The continuing division in opinion regarding the formal oxidation state of these cerium compounds has led us to perform a CASPT2 study of $CePn_2$. We have recently carried out similar studies of cerocene, thorocene and protactinocene [11], and find that in the case of cerocene strong hybridization between the metal f_δ and ligand $\pi(e_{2u})$ levels can lead to an ambiguous interpretation of the degree of 'f^1' character in the ground state wavefunction in terms of configurational admixture. We instead use the natural orbital occupations [25] (NOOs) along with the corresponding natural orbitals (NOs) in order to interpret the multiconfigurational nature of the cerocene ground state and obtain a value for the total f occupation, n_f. We find active space NOOs of 1.751 and 0.216 for the 'ligand' and 'metal' NOs of e_{2u} symmetry, respectively. Such deviation from integer occupation is an indicator of strong multiconfigurational character [26], yet under the assumption of localized orbitals, in which there is no hybridization between the ligand and metal e_{2u} levels, yields an n_f value of only = 0.43. The natural orbitals, however, show approximately 20% metal character in the 'ligand' level and *vice versa*. Taking this hybridization into account allows us to calculate a revised value of $n_f = 0.90 \pm 0.04$, in excellent agreement with that found experimentally [21], yet without near-integer occupation of a localised f_δ level.

In this contribution, we apply the same high-level methodology we have successfully employed on cerocene to establish if a similar description of the ground state is appropriate for $CePn_2$.

2. Computational details

The Gaussian 03 code [27] was used to investigate $CePn_2$ at the DFT level, using the TPSS exchange-correlation functional [28]. All results from DFT calculations were obtained using the small core SDD pseudopotential [29] and associated basis set for cerium, and the cc-pVDZ set [30] for carbon and hydrogen.

Complete active space self-consistent field (CASSCF) [31] calculations were performed using the MOLCAS 6.4 code [32], and dynamic correlation was accounted for using complete active space second order perturbation theory (CASPT2) [33]. Details of the active spaces employed for both the D_{2h} and D_{2d} isomers are given in the main text (and Tables 2 and 4). For the D_{2h} isomer, the number of orbitals kept frozen in each irrep during the CASPT2 procedure were: a_g: 11, b_{1g}: three, b_{2g}: four, b_{3g}: four, a_u: one, b_{1u}: six, b_{2u}: five, b_{3u}: five. For the D_{2d} isomer which, as discussed in the main text, was calculated in the C_{2v} point group, the number of orbitals kept frozen in each irrep during the CASPT2 procedure were: a_1: 17, a_2: four, b_1: nine, b_2: nine.

Scalar relativistic effects were included using the second order Douglas-Kroll Hamiltonian [34], whereas spin-orbit coupling, which we have previously shown to be very weak in $CeCOT_2$ [11], was neglected. All electron ANO basis sets were used for these calculations. For cerium, the ANO set was constructed by Roos [35], contracted as (25*s*22*p*15*d*11*f*)/[9*s*8*p*5*d*4*f*], and is of approximate cc-VQZ quality. The basis sets were of cc-pVDZ quality for C and H. This basis set combination has been shown [11] to produce results of comparable accuracy to those obtained using sets of cc-pVQZ quality for Ce and of cc-pVTZ quality for C and H. To aid comparison with CASPT2 results, MOLCAS 6.4 was also used to perform DFT calculations using the B3LYP exchange-correlation functional [36] and the same ANO basis in order to consider the differences in f-orbital occupation when using the CASPT2 and DFT methods.

3. Results and discussion

3.1. DFT study

Crystalline $CePn'_2$ ($Pn' = C_8H_4(Si^iPr_3\text{-}1,4)$) is found to contain two distinct conformers [9], which can be characterized in terms of the twist angle, *i.e.* the angle between the bridgehead C-C bonds in the two Pn′ ligands. One of the conformers is approximately staggered, with a twist angle of 85.0°, whilst the other is semieclipsed, with a twist angle of 33°. The situation is similar in $CePn^*_2$ ($Pn^* = C_8Me_6$), where three conformers are reported [10]: an approximately staggered conformer with twist angle of 79.8°, and two semieclipsed conformers with twist angles of 20.1 and 40.1° respectively. Bearing this in mind, the $CePn_2$ structure was optimized using the Gaussian 03 code within the constraints of the D_2, D_{2d} and D_{2h} point groups. The D_2-constrained optimization resulted in a structure of D_{2d} symmetry, and this structure was found to be a minimum. The D_{2h} structure was found to have one imaginary frequency at $i35.9\ cm^{-1}$, and to lie 0.13 eV (12.5 kJ/mol) higher in energy. These results are in good agreement with previous DFT work [9] using the B3LYP and BP86 [36,37] exchange-correlation functionals. Table 1 summarises relevant parameters of the optimized D_{2d} structure. There is good general agreement between the optimized structure obtained here and those found previously [9,10], with TPSS giving a slightly reduced Ce-C(β) separation and corresponding increased ligand fold angle.

We find the DFT calculated electronic structure of the D_{2d} conformer to be as reported previously [9,10]. The ground

Table 1
Structural parameters for calculated $CePn_2$ and synthesized substituted compounds.

Parameter	Calculated			Experimental	
	Ref [9]	Ref [10]	Present Work	$CePn'_2$ [9]	$CePn^*_2$ [10]
Ce-C (br)	2.51	-	2.50	2.49–2.52	-
Ce-C (α)	2.74	-	2.72	2.73–2.76	-
Ce-C (β)	2.88	-	2.86	2.89–2.93	-
$\overline{\text{Ce} - \text{C}}$	2.72	2.67	2.70	2.73	2.68
Ligand fold ∠	24.4	24.0	25.6	23.0	24.7
Twist ∠	87.72	90[a]	90[a] (90.04[b])	85.0	79.8

Quoted lengths are in Angstroms, and angles in degrees.

[a] Optimization performed under constraints of D_{2d} symmetry.

[b] Optimised twist angle, differing from 90° due to convergence criteria.

state is $^1A_1$, with the a_2 symmetry HOMO and b_1 HOMO-1 displaying significant f_δ and d_δ character respectively. The LUMO is of e-symmetry and is an almost completely localized f-level. The ground state of the higher energy D_{2h} conformer is analogous: the state symmetry is ^1A_g, with the a_u symmetry HOMO and b_{3g} HOMO-1 displaying significant f_δ and d_δ character respectively. The lowest lying unoccupied levels are localized f-levels. We defer consideration of the degree of f-character in the ground state until Section 3.2.3, where comparison is made between DFT and CASPT2 calculations using identical basis sets.

3.2. CASPT2 study

CASPT2 calculations were performed on both the D_{2h} and D_{2d} conformers at the TPSS-optimised geometries. In the case of the D_{2d} conformer, computational restrictions enforced in MOLCAS required calculations to be performed in the C_{2v} point group (an Abelian subgroup of D_{2d}). Such a reduction in symmetry can, in principle, allow mixing of orbitals that would be forbidden in the full point group, and such mixing was monitored and eliminated during the calculations. Throughout the remainder of this study we will refer to orbitals and states in terms of their C_{2v} symmetry labels and, where appropriate, will give the corresponding D_{2d} labels in parentheses. In the case of the D_{2h} conformer, the full point-group could be employed in the calculations, and so no complication arises.

Although $CePn_2$ can be considered to be analogous to $CeCOT_2$, we have used a larger active space in the present calculations than was used in our $CeCOT_2$ study. In the previous study, an active space explicitly correlating eight

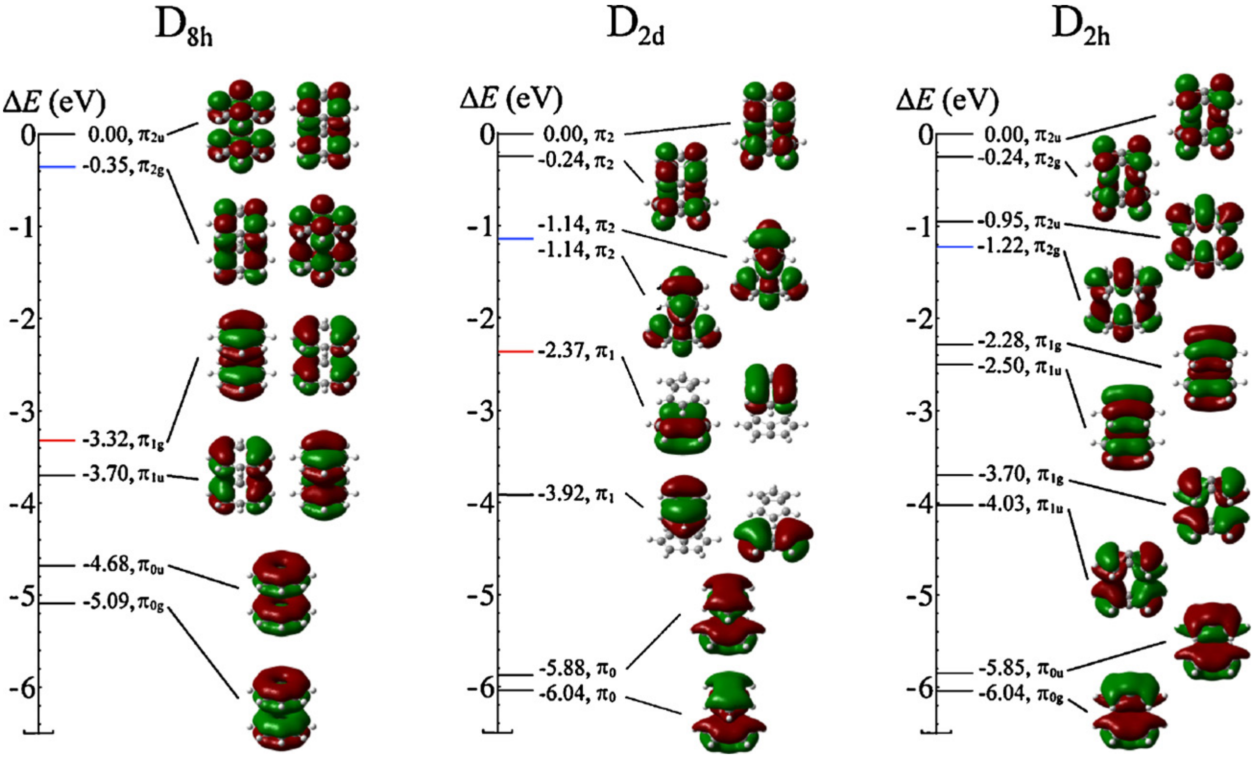

Fig. 1. Energy levels and molecular orbitals of COT_2^{4-} and the D_{2h} and D_{2d} conformers of Pn_2^{4-}. The blue and red levels indicate the lowest lying π_2 and highest lying π_1 level respectively.

Table 2
The (12,16) active space used in the CASPT2 calculations on the D_{2d} conformer of $CePn_2$, defined in terms of the occupied and virtual IVO-RHF input orbitals within the C_{2v} point group.

	A_1	A_2	B_1	B_2
Inactive (occupied)	31	10	18	18
Active (occupied)	2	2	1	1
Active (virtual)	2	2	3	3

Table 3
Relative energies and maximum deviation from integer natural orbital occupancy (Δ_{NOO}) of the 16 CASPT2(12,16) calculated states of the D_{2d} isomer of $CePn_2$.

	Singlet		Triplet	
	Energy (eV)	Δ_{NOO}	Energy (eV)	Δ_{NOO}
A_1	0.00	0.391	1.16	0.054
	2.34	0.086	2.24	0.106
A_2	2.72	0.068	2.72	0.068
	3.19	0.072	3.21	0.073
B_1	0.87	0.054	0.88	0.054
	2.01	0.086	1.94	0.086
B_2	0.87	0.054	0.88	0.054
	2.01	0.086	1.94	0.086

electrons in 14 orbitals, denoted CASPT2(8,14), was used. This active space included the eight electrons occupying the highest energy π_2 ligand orbitals spanning the doubly degenerate e_{2u} and e_{2g} irreps of the D_{8h} point group, and was sufficient since the energy gap between these orbitals and those below them (π_1 orbitals of e_{1g} and e_{1u} symmetry) was large. The lower point groups employed here strongly affect the relative energies of these orbitals, resulting in a significant reduction in the π_2-π_1 energy gap when the $CePn_2$ complexes are considered. This effect is shown graphically for the tetra-anionic ligand systems in Fig. 1, where the π_2-π_1 energy gap reduces from 2.97 eV ($CeCOT_2$) to 1.06 eV ($CePn_2$, D_{2h}) and 1.17 eV($CePn_2$, D_{2d}), and led us to expand the active space in the present calculations to include the higher lying of the π_1 levels. We therefore present CASPT2(12,16) calculations, using our adopted notation. It should be noted that this active space allows for occupation of any of the twelve 4f and 5d levels.

3.2.1. *The D_{2d} conformer*

The two energetically lowest singlet and triplet states of each irrep of C_{2v} (the working point-group) were obtained at the CASPT2 level, using the active space defined in Table 2. Input orbitals were generated from a restricted Hartree-Fock (RHF) [38,39] calculation, with the improved virtual orbital (IVO) method [40] used to produce more compact virtual orbitals.

Our CASPT2 calculations find a $^1A_1$ ground state, in agreement with our DFT results. This state lies 0.87 eV below the doubly degenerate first excited state, of B_1/B_2 (E) symmetry and singlet multiplicity. We quantify the multiconfigurational character in terms of the natural occupation numbers; NOOs which deviate from integer values by more than 0.1 are indicative of a strongly multiconfigurational system [26]. Table 3 shows the energies and the largest deviation from integer orbital occupancy within the active space for each of the sixteen states we consider here. The ground state is strongly

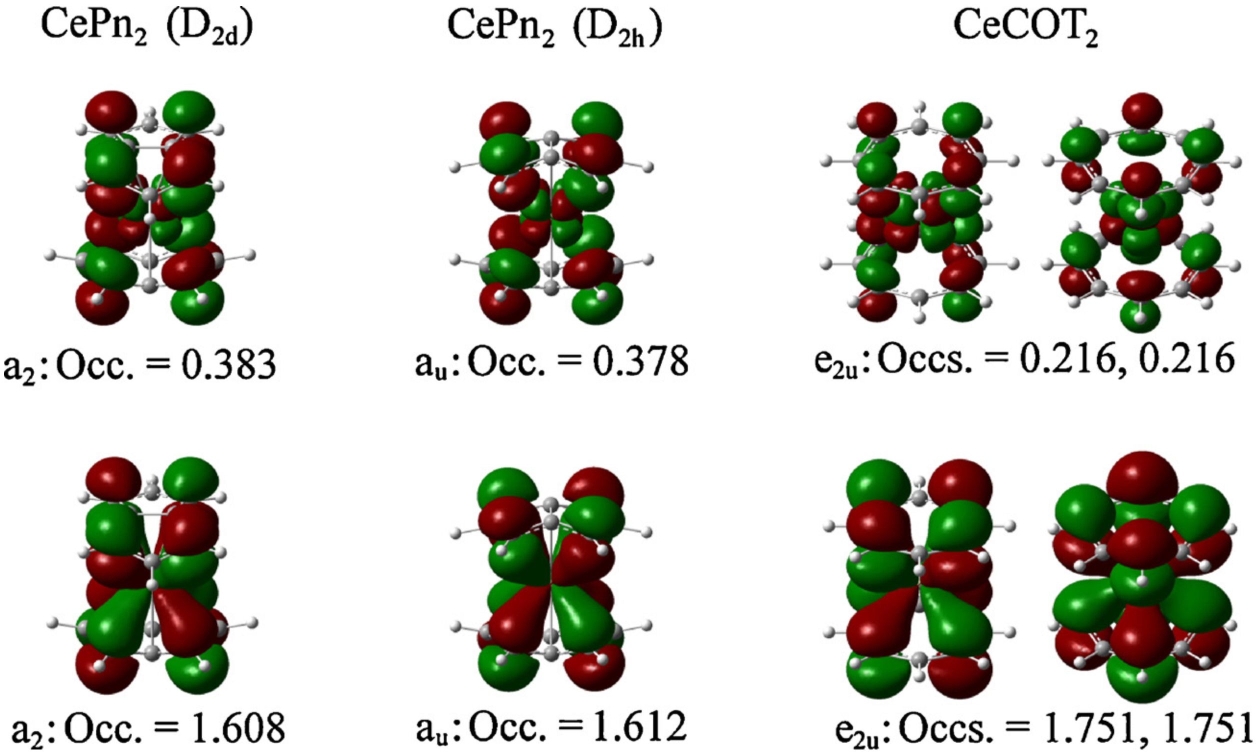

Fig. 2. $CePn_2$ ground state natural orbitals obtained from CASSCF(12,16) calculations, and $CeCOT_2$ ground state natural orbitals obtained from a CASSCF(8,14) calculation [11]. Only NOs with signifcantly non-integer occupation are shown.

Table 4
The (12,16) active space used in the CASPT2 calculations on the D_{2h} conformer of $CePn_2$, defined in terms of the occupied and virtual IVO-RHF input orbitals within the D_{2h} point group.

	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
Inactive (occupied)	18	6	7	9	4	13	11	9
Active (occupied)	1	1	1	0	1	1	0	1
Active (virtual)	1	1	1	1	1	1	2	2

multiconfigurational, with significant (0.383) occupation of the anti-bonding a_2 level of dominant f_δ character. This occupation is a direct result of the deoccupation of the corresponding bonding a_2 level (with a deoccupation of 0.391). This state bears a strong resemblance to that which we have previously reported as the cerocene ground state (as can be seen from the natural orbital diagrams of Fig. 2), with the difference here that the lower symmetry splits the degeneracy of the two f_δ orbitals, resulting in the multiconfigurational character being almost exclusively attributable to charge transfer between the bonding and antibonding a_2 orbitals with f_δ character, as opposed to contributions from both components of the doubly degenerate e_{2u} cerocene orbitals. The largest deviation from integer occupancy in the other active space orbitals is just 0.052, confirming the origin of the multiconfigurational character. By contrast to the CASPT2 ground state, the fifteen other states under consideration here have much lower multiconfigurational character. Again, this is strongly reminiscent of our cerocene results.

Experimentally, an "intense and broad absorption" is observed at 2.34 eV in the UV/Vis spectrum [10]. Time-dependent DFT calculations find a transition with oscillator strength $f = 0.071$ at an energy of 2.85 eV, due to excitation from a largely ligand based orbital with some Ce d_δ character into an Ce f_δ orbital, with the intensity of the transition arising from the d to f character of the transition [10]. Our CASPT2 calculations also identify this transition, but give better agreement with experiment. We find an oscillator strength of $f = 0.345$ for the transition, which we calculate to occur at 2.35 eV. Whilst this extremely good agreement is no doubt somewhat fortuitous, it again highlights the fact that multiconfigurational methods are required in order to model systems such as $CePn_2$ to a high level of accuracy.

Table 5
Relative energies and maximum deviation from integer natural orbital occupancy (Δ_{NOO}) of the 32 CASPT2(12,16) calculated states of the D_{2h} isomer of $CePn_2$.

	Singlet		Triplet	
	Energy (eV)	Δ_{NOO}	Energy (eV)	Δ_{NOO}
A_g	0	0.388	1.21	0.060
	2.36	0.194	3.96	0.710
B_{1g}	2.21	0.054	2.22	0.055
	2.78	0.578	2.55	0.561
B_{2g}	0.93	0.052	0.97	0.050
	2.08	0.066	2.11	0.061
B_{3g}	0.96	0.054	0.98	0.052
	2.09	0.066	2.10	0.054
A_u	1.60	0.241	1.60	0.231
	3.38	0.060	3.41	0.083
B_{1u}	2.45	0.087	2.30	0.109
	2.63	0.434	2.63	0.424
B_{2u}	2.18	0.076	2.06	0.085
	4.59	0.148	3.26	0.097
B_{3u}	2.13	0.092	2.01	0.093
	3.70	0.017	3.66	0.125

3.2.2. The D_{2h} conformer

The two energetically lowest singlet and triplet states of each irrep of D_{2h} were obtained at the CASPT2 level, using the active space defined in Table 4. Input orbitals were generated from a restricted Hartree-Fock (RHF) [38,39] calculation, with the improved virtual orbital (IVO) method [40] used to produce more compact virtual orbitals.

As with the G03 DFT calculations we find an ^1A_g ground state for the D_{2h} conformer. At the CASPT2 level this state lies 0.24 eV (23.2 kJ/mol) above the D_{2d} ground state. The D_{2h} ground state bears strong similarities to both that of the D_{2d} conformer and cerocene, i.e. a strongly multiconfigurational wavefunction resulting from the strong (0.378) occupation of the antibonding a_u orbital of dominant f_δ character. Again, this occupation results almost exclusively from deoccupation of the corresponding bonding a_u level (deoccupation of 0.388). The ground state is stable by 0.93 eV relative to the first excited state of $^1B_{2g}$ symmetry. The low lying excited states typically have only small deviations from integer occupancy, as is the case for the D_{2d} conformer (compare Tables 3 and 5). There are, however, several excited states (of B_{1g}, A_u and B_{1u} symmetry and both spin multiplicities) which are strongly multiconfigurational. These multiconfigurational excited states exhibit the strong occupation of the antibonding a_u orbital of dominant f_δ character, in common with the ground state, but also correspond to ligand to metal charge transfer excitations. This is in contrast to cerocene, where all excited states were found to be well described by a single-configuration wavefunction.

3.2.3. Evaluation of the f-density

Fig. 3a shows the variation in the configurational weights of the $\pi_{a_2}^2 f_\delta^0$ and $\pi_{a_2}^1 f_\delta^1$ [1]configurations in the D_{2d} conformer of $CePn_2$ when the size of the state average in the calculation is varied. This variation is marked, and shows that such weights are not a reliable measure of multiconfigurational character, as we found in our previous study of cerocene. Fig. 3b shows the corresponding natural orbital occupations, which are more robust with respect to the size of the state average, and which we use to calculate a value for the total f-density (n_f). We have described our approach for obtaining n_f in

---

[1] The used of inverted commas is to remind the reader that these orbitals are not localized, and the labels refer to dominant character.

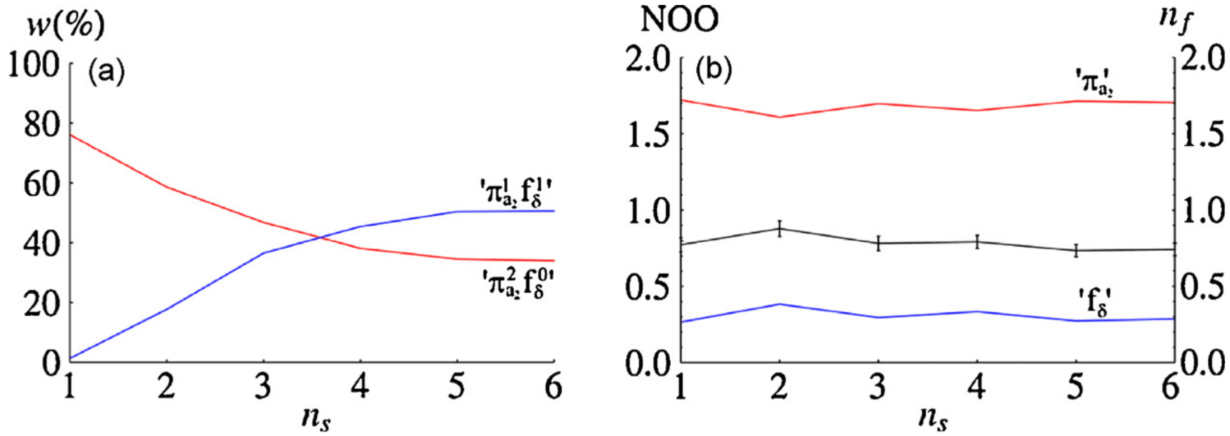

Fig. 3. (a) configurational weights and (b) natural orbital occupancies as a function of state average size (n_s) for the D_{2d} conformer of $CePn_2$. Also shown in (b) are the calculated f-densities (n_f).

detail elsewhere [11], and so will only briefly describe it here. We calculate the total f-contribution to each of the natural orbitals comprising the active space and multiply by the corresponding natural orbital occupation to obtain a value for the f-density. This procedure assumes the metal and ligand basis functions are orthogonal, which is not the case, but the error associated with this assumption can be estimated by consideration of the normalization constants of each orbital, and results in the error bars present in Fig. 3b. Our calculations suggest that an appropriate value of n_f for this system is 0.78 ± 0.04. This is a little smaller than the value we have previously calculated for cerocene (0.90 ± 0.04), and is in good agreement with that found experimentally by Ashley et al.; 0.87 ± 0.05 [10]. Our calculations show that the ground state of $CePn_2$ can be considered analogous to that of cerocene.

In order to compare this result with that obtained from a single-configuration DFT calculation, MOLCAS was used to generate a set of Kohn-Sham orbitals for $CePn_2$ using the B3LYP functional and the same basis set and molecular geometries as was used for the CASPT2 calculations. The D_{2d} conformer was again found to be the lowest energy structure, and was stable by 0.21 eV (20 kJ/mol) with respect to the D_{2h} conformer. Inspection of the Kohn-Sham orbitals for the D_{2d} conformer reveals the a_2 HOMO and LUMO to be almost indistinguishable from the partially-occupied natural orbitals shown in Fig. 2, and n_f is calculated to be 0.62 ± 0.01. This value, whilst significant, is substantially lower than that obtained from the natural orbitals, and is a result of the inability of the single-configurational method to represent the partial occupation of the a_2 LUMO of dominant f_δ character.

4. Summary and conclusions

$CePn_2$ has been shown experimentally [9,10] to bear a striking resemblance to cerocene, for which the debate as to the oxidation state of the cerium ion continues. We have shown computationally that the electronic structure of $CePn_2$ is extremely similar to that of cerocene, and that whilst multiconfigurational methods are required to accurately describe the ground state wavefunction, it is not dominated by a '$\pi^3 f_\delta{}^1$' configuration. Instead, our analysis *via* natural orbital occupancies suggests that $CePn_2$, like $CeCOT_2$ [11], is best described as a Ce(IV) system in which the transfer of electron density from ligand to metal through partial occupation of a metal dominated orbital results in a significant metal 4f density. This conclusion is not in conflict with the XANES data of [9,10]: in fact, our calculated value for the Ce ion f-density is in good agreement with that found experimentally. However, our analysis suggests that experimental measures of the effective (as opposed to formal) oxidation state cannot necessarily be used to unambiguously define the detailed electronic structure of complexes such as $CePn_2$.

Acknowledgements

We are grateful to the EPSRC for financial support (*via* grants EP/C533054 and GR/S06233) and for the use of its National Service for Computational Chemistry Software (http://www.nsccs.ac.uk). We also thank UCL for computing resources via the Research Computing "Legion" cluster and associated services.

References

[1] A.J. Streitwieser, U. Müller-Westerhof, J. Am. Chem. Soc 90 (1968) 7364.
[2] A. Streitweiser, N. Yoshida, J. Am. Chem. Soc 91 (1969) 7528.
[3] J.P. Solar, H.P.G. Burghard, R.H. Banks, A.J. Streitwieser, D. Brown, Inorg. Chem 19 (1980) 2186.
[4] D.G. Karraker, J.A. Stone, E.R. Jones, N. Edelstein, J. Am. Chem. Soc 92 (1970) 4841.
[5] A. Greco, S. Cesca, G. Bertolini, J. Organomet. Chem 113 (1976) 321.
[6] A. Streitwieser, S.A. Kinsley, J.T. Rigsbee, I.L. Fragala, E. Ciliberto, N. Rosch, J. Am. Chem. Soc 107 (1985) 7786.
[7] F.G.N. Cloke, P.B. Hitchcock, J. Am. Chem. Soc 119 (1997) 7899.
[8] F.G.N. Cloke, J.C. Green, C.N. Jardine, Organometallics 18 (1999) 1080.
[9] G. Balazs, F.G.N. Cloke, J.C. Green, R.M. Harker, A. Harrison, P.B. Hitchcock, C.N. Jardine, R. Walton, Organometallics 26 (2007) 3111.
[10] A. Ashley, G. Balazs, A. Cowley, J. Green, C.H. Booth, D. O'Hare, Chem. Commun (2007) 1515.
[11] A. Kerridge, R. Coates, N. Kaltsoyannis, J. Phys. Chem. A 113 (2009) 2896.

[12] R. Coates, M. Coreno, M. DeSimone, J.C. Green, N. Kaltsoyannis, A. Kerridge, N. Narband, A. Sella, Dalton Trans (2009) 5943.
[13] K.O. Hodgson, K.N. Raymond, Inorg. Chem 11 (1972) 171.
[14] K.N. Raymond, C.W. Eigenbrot, Acc. Chem. Res 13 (1980) 276.
[15] C.S. Neumann, P. Fulde, Z. Phys. B-Cond. Matt 74 (1989) 277.
[16] M. Dolg, P. Fulde, W. Kuechle, C.S. Neumann, H. Stoll, J. Chem. Phys 94 (1991) 3011.
[17] M. Dolg, P. Fulde, H. Stoll, H. Preuss, A. Chang, R.M. Pitzer, Chem. Phys 195 (1995) 71.
[18] W.J. Liu, M. Dolg, P. Fulde, J. Chem. Phys 107 (1997) 3584.
[19] W.J. Liu, M. Dolg, P. Fulde, Inorg. Chem 37 (1998) 1067.
[20] N.M. Edelstein, P.G. Allen, J.J. Bucher, D.K. Shuh, C.D. Sofield, N. Kaltsoyannis, G.H. Maunder, M.R. Russo, A. Sella, J. Am. Chem. Soc 118 (1996) 13115.
[21] C.H. Booth, M.D. Walter, M. Daniel, W.W. Lukens, R.A. Andersen, Phys. Rev. Lett 95 (2005) 267202.
[22] H.D. Amberger, H. Reddmann, F.T. Edelmann, J. Organomet. Chem 690 (2005) 2238.
[23] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) B864.
[24] W. Kohn, L.J. Sham, Phys. Rev 140 (1965) 1133.
[25] P.O. Löwdin, Phys. Rev 97 (1955) 1474.
[26] M.W. Schmidt, M.S. Gordon, Ann. Rev. Phys. Chem 49 (1998) 233.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. Montgomery, J. A., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 revision D.01, Gaussian, Inc., Wallingford CT, 2004.
[28] J.M. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Phys. Rev. Lett 91 (2003) 146401.
[29] M. Dolg, H. Stoll, H. Preuss, J. Chem. Phys 90 (1989) 1730.
[30] T.H. Dunning, J. Chem. Phys 90 (1989) 1007.
[31] B.O. Roos, P.R. Taylor, Chem. Phys 48 (1980) 157.
[32] G. Karlstrom, R. Lindh, P.A. Malmqvist, B.O. Roos, U. Ryde, V. Veryazov, P.O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, Comp. Mat. Sci 28 (2003) 222.
[33] K. Andersson, P.A. Malmqvist, B.O. Roos, A.J. Sadlej, K. Wolinski, J. Phys. Chem 94 (1990) 5483.
[34] M. Douglas, N.M. Kroll, Ann. Phys 82 (1974) 89.
[35] B.O. Roos, Unpublished.
[36] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[37] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[38] D.R. Hartree, Proc. Cam. Phil. Soc 24 (1928) 89.
[39] V.A. Fock, Ann. Phys. (Leipzig) 61 (1930) 126.
[40] W.J. Hunt, W.A. Goddard, Chem. Phys. Lett 3 (1969) 414.