Relativistic and Electron-Correlation Effects in the Ground States of Lanthanocenes and Actinocenes**

M. Dolg* and P. Fulde

Abstract: The sandwich complex $[Ce(C_8H_8)_2]$ has conclusively been shown to be a bis([8]annulene)cerium(III) complex by theoretical as well as experimental investigations. Its electronic ground state can only be understood by taking electron correlations into account. Fundamental differences between lanthanocenes and actinocenes as well as their anions result mainly from the greater effect of relativistic effects in the heavier actinide systems.

Keywords: ab initio calculations · actinides · electronic structure · lanthanides · sandwich complexes

Introduction

Among the bis([8]annulene)metal complexes $[M(C_8H_8)_2]$ of lanthanides (M = Ln) and actinides (M = An), that is, the so-called lanthanocenes and actinocenes, the molecules cerocene $[Ce(C_8H_8)_2]$ and thorocene $[Th(C_8H_8)_2]$ are of particular interest for the following reason. The general belief is that the two systems are isoelectronic and are characterized by a tetravalent central metal, as indicated by their experimentally observed diamagnetism. The conventional explanation is the closed-shell character resulting from the complexation of the Ce^{4+} $4f^0$ and Th^{4+} $5f^0$ ions by two aromatic $C_8H_8^{2-}$ ligands. However, it is well-known from solid-state physics that Ce^{3+} ions with a $4f^1$ configuration embedded in a metallic matrix can be in a singlet state,[1] that is, in a state with no magnetic moment. This feature is reflected in the spin susceptibility. Examples are $CeAl_3$, $CeCu_6$, $CeCu_2Si_2$ and many others. The singlet is formed by the 4f electron on the Ce^{3+} and an unpaired electron from the environment of the metal. This form of a ground-state wavefunction is associated with the name of Kondo (Kondo singlet)[2] and the associated energy gain ΔE is often expressed in terms of a temperature (Kondo temperature); $\Delta E = k_B T_K$. The Kondo temperature is often very small, namely of the order of tens of degrees. Therefore systems like $CeAl_3$ have a large number of low-energy excitations because the singlets are easily broken up. A whole branch of low-temperature physics has developed over the past twenty years devoted to the study of the various consequences of the formation of Kondo singlets. Returning to cerocene, the question arises as to whether the absence of paramagnetism in this molecule has its origin in the presence of a $4f^0$ configuration or, as in $CeAl_3$, in the formation of a singlet between a Ce^{3+} with a $4f^1$ configuration and an unpaired ligand π electron.

The high D_{8h} symmetry of these sandwich compounds allows us to study theoretically the individual contributions of the metal s (a_{1g}), p (a_{2u}, e_{1u}), d (a_{1g}, e_{1g}, e_{2g}) and f (a_{2u}, e_{1u}, e_{2u}, e_{3u}) valence orbitals to metal–ring bonding. Sometimes an idealized $D_{\infty h}$ point group is used to simplify the notation of the irreducible representations, that is, s (σ_g), p (σ_u, π_u), d (σ_g, π_g, δ_g)and f (σ_u, π_u, δ_u, ϕ_u). In fact, after the discovery of uranocene $[U(C_8H_8)_2]$ by Streitwieser and Müller-Westerhoff in 1968,[3] numerous studies of these f-element metallocenes were performed.[4–11] However, all these studies assumed systems with tetravalent central atoms, that is, in a simplified, completely ionic limit a $M^{4+}(C_8H_8^{2-})_2$ charge distribution with two aromatic ligands (10 π electrons each) and, at the beginning of each series, a closed-shell central ion (Ce^{4+}, Th^{4+}). The highest occupied π orbitals of the $C_8H_8^{2-}$ ligands form e_{2g} and e_{2u} linear combinations in the metallocenes, and are involved in the main covalent interactions with the empty central ion d and f valence orbitals of the same character (δ_g and δ_u, respectively). The correct assignment of the photoelectron spectra as well as their interpretation in terms of individual orbital contributions to metal–ring bonding was a major step towards the understanding of the electronic structure of lanthanocenes and actinocenes.[8,12]

In the case of the actinocenes $[An(C_8H_8)_2]$, so far only the experimentally known systems[13] containing central metals from the first third of the series have been investigated theoretically (An = Th, Pa, U, Np, Pu). Relativistic density

---

[*] Dr. M. Dolg, Prof. Dr. P. Fulde
Max-Planck-Institut für Physik komplexer Systeme
Nöthnitzer Str. 38, D-01187 Dresden (Germany)
Fax: Int. code +(49) 351 871-2199
e-mail: dolg@mpipks-dresden.mpg.de

[**] Although IUPAC recommends restriction of metallocene nomenclature to cyclopentadienyl complexes, for the sake of simplicity the expressions lanthanocene, actinocene and so on are used in this paper for sandwich complexes of C_8H_8.

0947-6539/98/0402-0200 $ 17.50+.50/0

functional and intermediate neglect of differential overlap (INDO) calculations found the 6d orbitals to be equally or even more important than the 5f orbitals in the covalent metal–ring bonding in the case of thorocene, while for the later actinocenes the 5f contributions become dominant.[7,9,11] Hartree–Fock calculations using relativistic pseudopotentials found the 6d orbitals to be more important than the 5f orbitals in the case of uranocene too,[10] in agreement with photoelectron spectroscopy.[12] The subjacent ligand π orbitals form e_{1g} and e_{1u} linear combinations in the metallocenes, of which the former have a weaker, but nonnegligible, covalent interaction with the metal d orbitals (π_g).[4]

Among the lanthanocenes $[Ln(C_8H_8)_2]$, so far only cerocene (Ln = Ce) has been examined both theoretically and experimentally.[6–8] Despite the rather compact nature of the Ce 4f orbitals a considerable covalent metal–ring interaction was detected,[7] and the coexistence of a strong reducing agent ($C_8H_8^{2-}$) and a powerful oxidizing agent (Ce^{4+}) in form of a simple ionic cluster was doubted.[8] Nevertheless, in the literature cerocene and its derivatives are considered to be bis([8]annulene)cerium(IV) complexes.[8,14–16]

As pointed out above, in analogy to a Ce^{3+} Kondo ion in a metal,[1] cerocene was proposed to have mainly the character of a trivalent central cerium metal ion, that is, a $Ce^{3+}(C_8H_8^{1.5-})_2$ charge distribution corresponding to a $4f^1\pi^3$ configuration, to a first approximation.[17] On the basis of semiempirical INDO calculations treating Ce as a point charge, the $4f^0\pi^4$ configuration corresponding to the $Ce^{4+}(C_8H_8^{2-})_2$ charge distribution was estimated to be about 10 eV higher in energy. The two unpaired electrons in the cerium 4f orbital, which resembles an atomic orbital, and the highest ligand π orbital may be coupled to form a singlet or a triplet, where the latter is found to be lower in energy at the single configurational level, in other words, when electron correlations are not taken into account. However, in the singlet state configuration interaction between $4f^1\pi^3$ and $4f^0\pi^4$ may occur, leading to a singlet ground state about 6 meV below the triplet state. It was speculated that replacing the conduction band coupled to a Ce^{3+} $4f^1$ Kondo ion in a solid by the partially filled π orbital extending over the two anionic [8]annulene rings would lead to a molecular Kondo system with special properties such as a temperature-dependent magnetic moment (zero and nonzero magnetic moment in the singlet ground and low-lying triplet excited state, respectively).

Subsequent large-scale ab initio calculations including relativistic effects by means of energy-consistent pseudopotentials as well as electron correlation effects at the multireference averaged coupled-pair functional level revealed that qualitatively this picture of cerocene as a bis([8]annulene)cerium(III) complex is correct, but that quantitatively the singlet–triplet splitting is about two orders of magnitude larger owing to the smaller energetic separation between the dominating $4f^1\pi^3$ and the admixed $4f^0\pi^4$ configuration.[18,19] Because of the singlet character of the ground state and the large singlet–triplet splitting, the oxidation state of the central metal cannot be determined by magnetic measurements. Finally, the experimental proof of a cerium atom with oxidation state III in cerocene was achieved by X-ray absorption near-edge structure (XANES) spectroscopy in 1996.[20] The K edge shifts of systems with tetravalent cerium were found at energies about 7 eV higher than those of trivalent cerium, including two substituted cerocenes. We note that the relativistic 1s orbital energies of atomic cerium in the $4f^15d^16s^2$ and $5d^26s^2$ configuration differ by 7.38 eV at the Hartree–Fock level, that is, the XANES measurements are indeed diagnostic for the 4f occupation number and the related oxidation state.

Abstract in German: *Durch theoretische und experimentelle Untersuchungen wurde eindeutig gezeigt, daß* $[Ce(C_8H_8)_2]$ *ein Bis([8]annulen)Cer(III)-Komplex ist. Sein elektronischer Grundzustand ist nur bei Berücksichtigung der Elektronenkorrelation zu verstehen. Grundlegende Unterschiede zwischen Lanthanoid- und Actinoid-Sandwichkomplexen sowie ihren Anionen sind hauptsächlich auf die größeren relativistischen Effekte bei den schwereren Actinoidsystemen zurückzuführen.*

Almost thirty years after the first synthesis of uranocene, many questions concerning the electronic structure of bis([8]annulene)f-element complexes still remain open. Why is cerocene the only neutral lanthanocene known experimentally, whereas the corresponding salts of the anionic lanthanocenes, such as $K[Ln(C_8H_8)_2]$, are well-known even for the heavier lanthanides?[13,21] Why does thorocene, despite the fact that it is stable, obviously not form a corresponding anion, in contrast to cerocene? If the cerocene is indeed bis([8]annulene)cerium(III), whereas thorocene is rather bis([8]annulene)thorium(IV), what about the situation at the end of both series? Despite fast progress in computer technology and software development, systems with f elements still pose a considerable challenge to quantum chemistry. However, the improved knowledge about the importance of shell structure, and relativistic and electron correlation effects in lanthanide[22,23] and actinide[23,24] compounds may serve as a basis for at least some tentative answers from theoretical studies. It is the goal of the present paper to summarize the recent results in this field.

Discussion

Atoms: Before we discuss the electronic structure of lanthanocenes and actinocenes, a short look at the central atoms is appropriate. Orbital energies ε and radial orbital expectation values $\langle r \rangle$ from nonrelativistic Hartree–Fock and relativistic Dirac–Hartree–Fock atomic calculations are shown in Figures 1 and 2, respectively, for the elements at the beginning and the end of both series (Ce and Lu; Th and Lr). It is well-known[25] that relativistic effects destabilize and expand the valence d and f orbitals, whereas they stabilize and contract the valence s (and p) orbitals. The shell-structure effect of stabilization due to incomplete shielding of the increased nuclear charge by the added electrons when going from left to right across the periodic table is especially large for the valence orbitals with the smallest main quantum number in a given element, for example 4f > 5d > 6s for lanthanides and 5f > 6d > 7s for actinides. From a geometrical point of view ($\langle r \rangle$)the Ln 4f and to a lesser extent the An 5f orbitals appear to

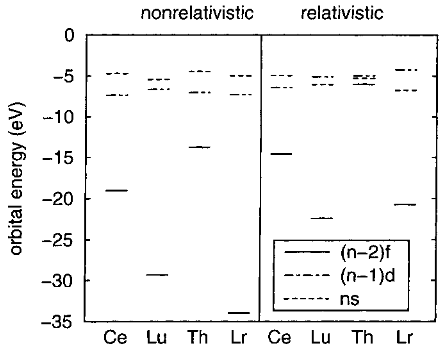

Figure 1. Nonrelativistic and spin–orbit-averaged relativistic orbital energies for Ce, Lu, Th and Lr from Hartree–Fock and Dirac–Hartree–Fock calculations.

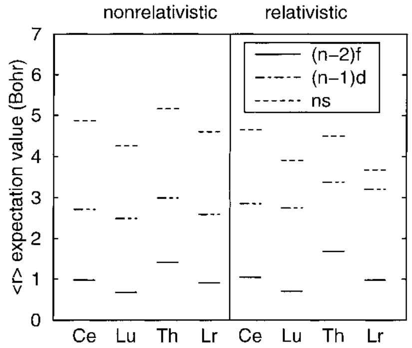

Figure 2. Nonrelativistic and spin–orbit-averaged relativistic orbital radius expectation values for Ce, Lu, Th and Lr from Hartree–Fock and Dirac–Hartree–Fock calculations.

be rather corelike; they are shielded from the spatial valence region by filled 5s,5p and 6s,6p shells, respectively. However, according to energetic considerations (ε), the 5f orbitals at the beginning of the actinide series behave as real valence orbitals, mainly owing to large destabilizing relativistic effects. Whereas Ce ($4f^1 5d^1 6s^2$) and Th ($6d^2 7s^2$) have different ground-state configurations because of the different impact of relativistic effects, this is not the case for Lu ($4f^{14} 5d^1 6s^2$) and Lr ($5f^{14} 6d^1 7s^2$), in which the stabilizing shell-structure effects dominate and lead to the complete filling of the f shell. This means that Ce^{III} and Th^{IV} as well as Lu^{III} and Lr^{III} are formally obtained by removing the electrons from the diffuse and therefore chemically accessible valence s and d orbitals.

Simple molecules: The differences between Ce and Th also affect the electronic structure of simple molecules;[23] for example, the CeO ground-state configuration is $4f\phi^1 6s\sigma^1$, whereas for ThO it is $7s\sigma^2$. It is noteworthy that it takes two electronegative oxygen ligands to remove the unpaired electron from the Ce 4f orbital, that is, formally CeO_2 and ThO_2 both have an unoccupied f valence shell, which contributes significantly to covalent chemical bonding.

Lanthanocenes: Relativistic ab initio pseudopotential calculations of selected lanthanocenes $[Ln(C_8H_8)_2]$ (Ln = Ce, Nd, Tb, Yb) indicate that all systems correspond to bis([8]annulene)lanthanide(III) compounds with leading $4f^n\pi^3$ configurations ($n = 0-14$ for La–Lu).[26] At the correlated level the configurations $4f^{n-1}\pi^4$ and $4f^{n+1}\pi^2$ may mix in and lead to a lower-than-maximum spin multiplicity in the ground state. In fact this has been found for cerocene ($^1A_{1g}$), neodymocene ($^3E_{3g}$) and terbocene ($^6E_{2u}$) (Table 1), whereas at the end of the series the energy lowering was too small for ytterbocene ($^3B_{2g}$). The energetic splitting between the two lowest states of different multiplicity decreases from 0.66 eV for cerocene ($^1A_{1g}-{}^3E_{2g}$) to less than 0.01 eV for ytterbocene ($^3B_{2g}-{}^1A_{2g}$). The reason appears to be the increasing corelike character of the 4f shell along the lanthanide series and as a consequence the weakening of both the metal–ligand exchange interaction within the leading $4f^n\pi^3$ configuration and the configuration interaction of $4f^n\pi^3$ with $4f^{n-1}\pi^4$ and $4f^{n+1}\pi^2$.

Table 2. Electronic structure of anionic bis([8]annulene)metal complexes $[M(C_8H_8)_2^-]$ from multireference averaged coupled-pair functional calculations with scalar relativistic pseudopotentials.

M	$_{58}$Ce	$_{60}$Nd	$_{90}$Th	$_{92}$U
m.c.[a]	$4f^1\pi^4$	$4f^3\pi^4$	$6d^1\pi^4$	$5f^3\pi^4$
g.s.[b]	$^2A_{2u}$	$^4E_{3u}$	$^2A_{1g}$	$^4E_{3u}$
EA[c]	1.39	2.11	−0.03	0.69
d[d]	2.18	2.19	2.21	2.17
ω_e[e]	185	183	190	187

[a] m.c.: Molecular ground state configuration. [b] g.s.: Molecular ground state. [c] EA: Adiabatic electron affinity of the neutral system (eV). [d] d: Metal–ring distance (Å). [e] ω_e: Symmetric metal–ring stretching frequency (cm^{-1}).

It should be noted that in case of cerocene, bis([8]annulene)cerium(III), the $^1A_{1g}$ ground state found at the multiconfiguration self-consistent field level for the 80:20 mixture of the $4f^1\pi^3$ and $4f^0\pi^4$ configurations[19] is identical to the ground state which must result for the $4f^0\pi^4$ configuration alone, bis([8]annulene)cerium(IV). Thus it is difficult to distinguish between the two possibilities cerium(III) and cerium (IV) on the basis of magnetic measurements. Terbocene is a candidate for a structure with a tetravalent central metal for which magnetic measurements should be able to make a decision between terbium(III) and terbium(IV), provided it is possible to synthesize the compound. Concerning this point a conversion similar to the one of $K[Ce(C_8H_8)_2]$ into $[Ce(C_8H_8)_2]$ with silver iodide[8] or allyl bromide[13] should in principle also be possible for the other lanthanocenes, provided slightly stronger oxidizing agents are used (Table 2).

Table 1. Electronic structure of neutral bis([8]annulene)metal complexes $[M(C_8H_8)_2]$ from multireference averaged coupled-pair functional calculations with scalar relativistic pseudopotentials.

M	$_{58}$Ce	$_{60}$Nd	$_{90}$Th	$_{92}$U
m.c.[a]	$4f^1\pi^3$	$4f^3\pi^3$	$5f^0\pi^4$	$5f^2\pi^4$
g.s.[b]	$^1A_{1g}$	$^3E_{3g}$	$^1A_{1g}$	$^3E_{3g}$
e.s.[c]	$^3E_{2g}$	$^5E_{3g}$	$^3E_{2u}$	$^1E_{3g}$
T[d]	0.66	0.18	2.17	0.69
d[e]	2.11	2.16	2.11	2.05
ω_e[f]	178	174	213	221

[a] m.c.: Molecular ground-state configuration. [b] g.s.: Molecular ground state. [c] e.s.: First excited state with higher or lower spin multiplicity. [d] T: Adiabatic term energy of e.s. (eV). [e] d: Metal–ring distance (Å). [f] ω_e: Symmetric metal–ring stretching frequency (cm^{-1}).

The electron affinity relating the as yet unknown neutral systems to the well-known anions is more or less constant for the heavier lanthanocenes (2.1 – 2.2 eV at the configuration interaction level) and about 0.7 eV higher than in the case of cerocene. The almost metal-independent values in the case of the heavier lanthanocenes result from the addition of the excess electron into the partially occupied ligand e_{2u} orbital. The reason for the low value for cerocene appears to be the strong stabilization of the neutral system due to the above-mentioned configuration-interaction mechanism.

Actinocenes: In contrast to the lanthanocenes, all actinocenes studied so far appear to be bis([8]annulene)metal(IV) systems. However, no central metal heavier than plutonium was considered, and the electronic structure of actinocenes from the second half of the series is a matter for speculation. It is obvious from the atomic orbital energies (Figure 1) that the 5f shell is strongly stabilized, whereas the 6d shell is slightly destabilized along the series. Shell-structure effects influence the 5f shell more strongly than the more diffuse 6d shell and overcompensate for the destabilisation by indirect relativistic effects. Since the Lr 5f shell is actually considerably deeper in energy than the Ce 4f shell, it is likely that $[Lr(C_8H_8)_2]$ corresponds to bis([8]annulene)lawrencium(III). Relativistic density functional calculations for the tetravalent light actinocenes $[An(C_8H_8)_2]$ (An = Th, Pa, U, Np, Pu) yield a reduction of the energy gap between the highest occupied ligand e_{2u} orbital and the lowest orbital of the empty or partially filled 5f shell from almost 3 eV in thorocene to less than 1 eV in plutonocene. Whereas the actinocenes in the first half of the series are bis([8]annulene)actinide(IV) complexes, it is to be expected that those of the second half are bis([8]annulene)actinide(III) compounds with an electronic structure very similar to the lanthanocenes. The electron affinity of the early actinocenes is probably metal-dependent and increases along the series, since the excess electron goes into the metal 6d or 5f shell. Large-scale ab initio pseudopotential calculations at the multiconfiguration-averaged coupled-pair functional level did not yield a positive electron affinity for thorocene (Table 2) but indicated that a $6d^1$ configuration would probably be more stable than a $5f^1$ configuration in the anion. In the case of uranocene, a positive electron affinity was calculated and the anion with a $5f^3$ configuration was found to be stable. Both findings are in agreement with the experimental existence of the salts $K[An(C_8H_8)_2]$ (An = U, Np, Pu, Am).[13] All actinocenes heavier than uranocene should readily form anions and for the second half of the series exhibit a metal-independent electron affinity similar to the lanthanocenes.

Closing Remarks

Any discussion of atomic or molecular electronic structure in terms of orbitals and single configurations, in other words, in terms of the independent-particle picture, is a simplification, which works in many but not in all cases. In the framework of the variational principle the best possible independent-particle description is obtained by the Hartree – Fock wavefunction yielding the lowest total energy. The theoretical assignment of oxidation states to central metals in organometallic complexes is based on the presence of well-localized (or localizable) orbitals resembling atomic orbitals within an independent-particle description, and becomes rather difficult or even meaningless when the latter breaks down. If we go beyond the independent-particle picture by taking into account electron correlations, using a multiconfigurational wavefunction and configuration interaction, we improve the theoretical description, but sacrifice the intuitive molecular orbital models. Therefore, it is often useful to characterize the system by means of only the leading Hartree – Fock part of the correlated wavefunction. A notable demonstration for these statements is the unusual ground state of cerocene. Although qualitatively, considering for example the spin and spatial symmetry of the ground state, the compound behaves like a bis([8]annulene)cerium(IV) complex, the cerium central metal actually has an oxidation state much closer to III than to IV, and the complex should therefore be described as a bis([8]annulene)cerium(III) compound. Electron correlations—at least a two-configurational description including $4f^1\pi^3$ (80%) and $4f^0\pi^4$ (20%)—are necessary to explain the singlet and totally symmetric character of the $^1A_{1g}$ ground state. Note that the configuration interaction is only possible when the occupied f orbital of the metal and the ligand orbital carrying the hole are of the same symmetry. It is expected that similar situations might occur in other cerium systems with extended ligands of low electronegativity; however, theoretical investigations as well as the interpretation of experimental data are often less easy because of the lower symmetry. Further experimental investigations are needed to confirm the postulated existence of neutral lanthanocenes other than cerocene. Rather involved studies with short-lived radioactive isotopes would be necessary to establish the change from bis([8]annulene)actinides(IV) to bis([8]annulene)actinides(III) near the middle of the actinide series. Theoretical investigations using modern quantum-chemical methods to account for electron correlation as well as relativistic effects might be a promising alternative.

Received: July 8, 1997 [C759]

---

[1] P. Fulde, *Electron Correlations in Molecules and Solids*, *Springer Series in Solid-State Sciences, Vol. 100*, Springer, Berlin, **1991**.

[2] J. Kondo, *Prog. Theor. Phys.* **1964**, *32*, 37.

[3] A. Streitwieser, U. Müller-Westerhoff, *J. Am. Chem. Soc.* **1968**, *90*, 7364.

[4] N. Rösch, A. Streitwieser, *J. Organomet. Chem.* **1978**, *145*, 195.

[5] P. Pyykkö, L. L. Lohr, *Inorg. Chem.* **1981**, *20*, 1950.

[6] N. Rösch, A. Streitwieser, *J. Am. Chem. Soc.* **1983**, *105*, 7237.

[7] N. Rösch, *Inorg. Chem.* **1984**, *94*, 297.

[8] A. Streitwieser, S. A. Kinsley, J. T. Rigsbee, I. L. Fragala, E. Ciliberto, N. Rösch, *J. Am. Chem. Soc.* **1985**, *107*, 7786.

[9] P. M. Boerrigter, E. J. Baerends, J. G. Snijders, *Chem. Phys.* **1988**, *122*, 357.

[10] A. H. H. Chang, R. M. Pitzer, *J. Am. Chem. Soc.* **1989**, *111*, 2500.

[11] M. G. Cory, S. Köstlmeier, M. Kotzian, N. Rösch, M. C. Zerner, *J. Chem. Phys.* **1994**, *100*, 1353.

[12] J. P. Clark, J. C. Green, *J. Chem. Soc. Dalton Trans.* **1977**, 505.

[13] A. Streitwieser, T. R. Boussie, *Eur. J. Solid-State Inorg. Chem.* **1991**, 28, 399.

[14] T. R. Boussie, D. C. Eisenberg, J. Rigsbee, A. Streitwieser, A. Zalkin, *Organometallics* **1991**, *11*, 1922.

[15] R. D. Fischer, *Angew. Chem.* **1994**, *106*, 2253; *Angew. Chem. Int. Ed. Engl.* **1994**, *106*, 2165.

[16] F. T. Edelmann, *Angew. Chem.* **1995**, *107*, 2647; *Angew. Chem. Int. Ed. Engl.* **1995**, *107*, 2466.

[17] C.-S. Neumann, P. Fulde, *Z. Phys. B* **1989**, *74*, 277.

[18] M. Dolg, P. Fulde, W. Küchle, C.-S. Neumann, H. Stoll, *J. Chem. Phys.* **1991**, *94*, 3011.

[19] M. Dolg, P. Fulde, H. Stoll, H. Preuss, R. M. Pitzer, A. Chang, *Chem. Phys.* **1995**, *195*, 71.

[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.* **1996**, *118*, 13115.

[21] K. O. Hodgson, F. Mares, D. F. Starks, A. Streitwieser, *J. Am. Chem. Soc.* **1973**, *95*, 8650.

[22] M. Dolg, H. Stoll, in *Handbook of Chemistry and Physics of Rare Earths, Vol. 22* (Eds.: K. A. Gschneidner, L. Eyring), Elsevier, Amsterdam, **1996**, 607.

[23] M. Dolg, in *Encyclopedia of Computational Chemistry* (Eds.: N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollmann, H. F. Schaefer), John Wiley, New York, in press.

[24] M. Pepper, B. C. Bursten, *Chem. Rev.* **1991**, *19*, 719.

[25] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

[26] W. Liu, M. Dolg, P. Fulde, *J. Chem. Phys.* **1997**, *107*, 3584.

0947-6539/98/0402-0204 $ 17.50+.50/0