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Do f Electrons Play a Role in the Lanthanide−Ligand Bonds? A DFT Study of $Ln(NR_2)_3$; R = H, SiH_3

Laurent Maron* and Odile Eisenstein*,†

Laboratoire de Structure et de Dynamique des Systèmes Moléculaires et Solides, UMR 5636,
Université de Montpellier II, CC 14, Place Eugène Bataillon, 34095 Montpellier, Cedex 5, France

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The participation of 4f electrons in the bonding of the lanthanide complexes $Ln(NR_2)_3$; R = H, SiH_3, has been investigated at the DFT level. Structural parameters obtained with small core (f electrons in the valence) and large core (f electrons in the core) effective core potentials (ECPs) suggest the nonparticipation of the f electrons to the Ln−N bonding. A methodological study has been carried out on the lanthanide contraction with various ab initio methods using large core ECPs. The calculated lanthanide contraction (0.180 Å) is in excellent agreement with the experimental value (0.179 Å). Comparison of calculated structural parameters with available X-ray data shows that calculations with large core ECPs and density functional methods quantitatively reproduce the bonding at the lanthanide.

Introduction

Understanding the bonding to lanthanide and actinide is of increasing interest due in particular to the problem of separation in nuclear wastes. However, the number of theoretical studies of f elements has increased in the last years.[1] Whereas actinide complexes (e.g., AnO_2^{2+})[2−4] have been studied (see also ref 5), much less is known about lanthanide complexes. Calculations by Dolg et al.[6] on small molecules (diatomic molecules) and on the spectroscopy of lanthanocenes have been carried out. It has been shown that the atomic 4f shell of the lanthanide atom is strongly stabilized and does not contribute to the chemical bonding. Studies of large systems containing lanthanide centers have been limited, to our knowledge, to La and Lu[7] and thus did not address in details the role of 4f orbitals in the chemical bond since the atomic centers correspond to $4f^0$ and energetically low-lying $4f^{14}$ configuration, respectively. The very limited number of studies[8−11] of lanthanide complexes with open f shells is probably due to the complexity of the DFT calculations in the high spin configurations.

The present study addresses for the first time the role of f electrons in lanthanide-ligand bonds for the complete Ln series. Relativistic effects need to be incorporated at a proper level and several models are available in the case of molecular systems. A fully relativistic DFT calculation including four-component solutions is available with the Beijing code.[12] While this approach gives result in good agreement with experimental data, it is highly demanding in computational effort. An alternate solution is to solve the relativistic problem with the Douglas−Kroll[13,14] Hamiltonian in an all-electron scheme which is therefore limited to small systems. Effective core potentials (ECPs) that take into account implicitly the relativistic effects in a Schrödinger or Kohn-Sham calculation are necessary for calculating large systems.

In this paper, we have carried out a systematic investigation of a class of lanthanide compounds $Ln[N(SiR_3)_2]_3$; R = H, SiH_3 whose structures are known experimentally for R = $SiMe_3$.[15−19] Our focus was to determine the participation of the 4f electrons in the bonding and to select the most appropriate level of calculation which could reproduce properly the value of the lanthanide contraction and representative structural parameters. The contraction is experimentally determined by the following formula:

$$\Delta_{\text{lanthanide}} = R_e(\text{LaX}) - R_e(\text{LuX}) \tag{1}$$

and is found to be equal to 0.179 Å from experimental data.[20−22]

Computational Details

The calculations were carried out with the Gaussian 98 suite of programs.[23] The relativistic effective core potentials (RECPs), optimized by the Stuttgart−Dresden group,[24−26] were used for lanthanide centers and silicon. Large and small core RECPs were used. Small core RECPs include the n = 4, 5, 6 shells in the valence whereas the large core RECPs explicitly consider the 5s, 5p, 5d, 6s electrons in the valence shell and thus put the 4f electrons in the core. The large core RECPs were chosen according to the formal oxidation degree of the lanthanide center. Thus, 11 valence electron RECPs were used for the lanthanide III centers, 10 valence electron RECPs for lanthanide(II) (Eu, Yb), leading to a negatively charged complexes, and 12 valence electron RECPs for cerium(IV), leading to a positively charged complex. The RECPs were used in combination with their optimized basis sets, which were supplemented by polarization functions, namely, a g function for the small core lanthanide RECPs, an f function for the large core lanthanide ECP, and a d function on the silicon center. The carbon and the hydrogen atoms were treated with a 6-31G** basis set.

Geometry optimization at the Hartree-Fock (HF), MP2,[27] B3LYP,[28,29] and B3PW91[28,30] level of theory was carried out without any symmetry constraint. No spin−orbit interactions have been considered in the following.

Results and Discussion

Role of the 4f Electrons for $Ln(NH_2)_3$. In order to determine the influence of 4f electrons, results coming from small core (including explicitly the 4f shell in the valence) and large core RECPs at the B3PW91 (DFT) level are compared. The ground

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† E-mail: odile.eisenstein@lsd.univ-montp2.fr.

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TABLE 1: Ground State Configuration of $Ln(NH_2)_3$ Complexes Calculated at the B3PW91 Level

metal	configuration	oxidation deg	metal	configuration	oxidation deg
La	^1A	3	Tb	^7A	3
Ce	^1A	4	Dy	^6A	3
Pr	^3A	3	Ho	^5A	3
Nd	^4A	3	Er	^4A	3
Pm	^5A	3	Tm	^3A	3
Sm	^6A	3	Yb	^1A	2
Eu	^8A	2	Lu	^1A	3
Gd	^8A	3			

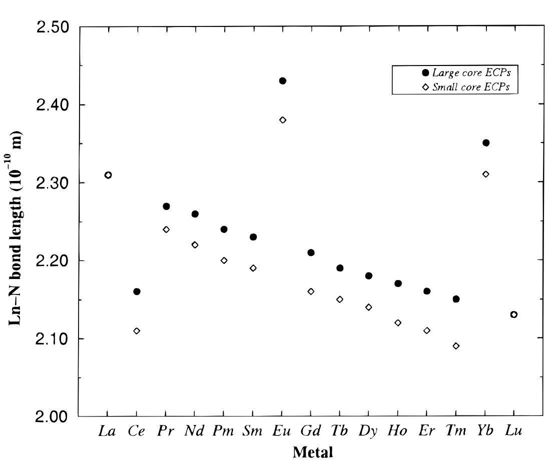

Figure 1. Ln-N bond lengths (Å) for $Ln(NH_2)_3$ complexes at the B3PW91 level.

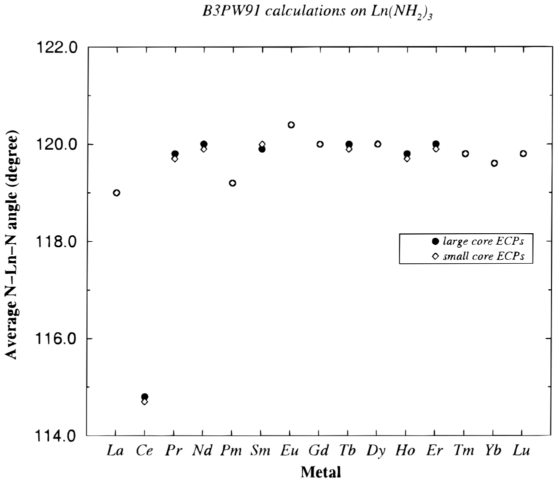

Figure 2. Average N−Ln−N bond angle (deg) for $Ln(NH_2)_3$ complexes at the B3PW91 level.

TABLE 2: Natural Ground State Configuration of $Ln(NH_2)_3$ Complexes Calculated at the B3PW91 Level

metal	configuration	natural configuration
La	^1A	6s(0.05)5d(0.42)6p(0.05)6d(0.02)
Ce	^1A	6s(0.06)4f(0.05)5d(0.42)6p(0.04)
Pr	^3A	6s(0.07)4f(2.02)5d(0.39)6p(0.04)5f(0.01)
Nd	^4A	6s(0.07)4f(3.01)5d(0.39)6p(0.03)5f(0.01)
Pm	^5A	6s(0.07)4f(4.04)5d(0.38)6p(0.04)5f(0.01)
Sm	^6A	6s(0.08)4f(5.03)5d(0.36)6p(0.04)5f(0.01)
Eu	^8A	6s(0.08)4f(7.01)5d(0.36)6p(0.04)5f(0.01)
Gd	^8A	6s(0.08)4f(7.05)5d(0.34)6p(0.04)5f(0.01)
Tb	^7A	6s(0.09)4f(8.06)5d(0.33)6p(0.03)5f(0.01)
Dy	^6A	6s(0.10)4f(9.07)5d(0.30)6p(0.04)5f(0.01)
Ho	^5A	6s(0.11)4f(10.05)5d(0.35)6p(0.04)5f(0.01)
Er	^4A	6s(0.11)4f(11.05)5d(0.41)6p(0.04)5f(0.01)
Tm	^3A	6s(0.11)4f(12.02)5d(0.57)6p(0.04)5f(0.01)
Yb	^1A	6s(0.11)4f(14.09)5d(0.60)6p(0.05)5f(0.01)
Lu	^1A	6s(0.15)5d(0.76)6p(0.07)6d(0.02)

state configuration of the open f-shell compounds was determined by calculating all possible spin occupations. Our calculations indicate that Hund's rule is obeyed for all complexes and the ground state configuration corresponds to the highest spin number (Table 1). This already suggests that the 4f electrons may not participate to the bonding. However, in order to obtain a more definite proof of this result, the Ln−N bond lengths (Figure 1) and average N−Ln−N angles (Figure 2) are compared for the two RECPs. The curves obtained with the small and large core RECPs are very similar (Figure 1). La($4f^0$) and Lu($4f^{14}$) are excluded from this comparison since no small core is available for these centers, which are in fact transition metal atoms. The Ln−N bond lengths are calculated to be slightly shorter (0.04 Å) with the small core RECPs than with the large core RECPs which is not due to a 4f participation to the bonding but could be probably attributed to a better treatment of the core-valence correlation with the small core RECPs. The lack of core polarization potential CPP[31,32] in our large core RECP calculation is in line with our analysis. The almost constant difference in bond lengths, 0.04 Å, with the two cores along the whole series suggests that the influence of the core−valence correlation on the geometry appears to be small. The nonparticipation of the 4f electrons to the bonding is also suggested from an NBO[33] analysis (Table 2) obtained from the small core ECP calculation. The number of electrons in the 4f shell is calculated to be equal to that in the isolated atom and entirely determines the total spin of the molecule as indicated by the configuration. Examination of bond order from the NBO analysis also proves that the 4f electrons remain in the atomic f orbitals. The calculated charge at the lanthanide center is very close to +3 for all atoms but Ce, for which it is +4, and Eu, Yb, for which it is +2. In all cases, the charge at nitrogen is close to −1. The bond appears to be strongly ionic with some slight donor−acceptor character.

The Ln−N bond length decreases monotonously (Figure 1) with increasing number of 4f electrons with the exception of Ce, Eu, and Yb. The shorter bond length in the case of Ce is associated with its formal oxidation state 4 and the smaller size of the Ce^{4+} ion. In the same way, Eu(II) and Yb(II) lead to longer bond lengths associated with a larger size of the Eu^{2+} and Yb^{2+} ions with respect to a Ln^{3+} ion. The angles N−Ln−N remain close to 120° (Figure 2) and the metal lies in the plane defined by the three nitrogens, with the exception of Ce in which a small pyramidalization is obtained.

The equivalent results obtained with large and small core RECPs is in good agreement with the experimental analysis by Anderson et al.[34] and more recently by King et al.[35] Anderson et al. have shown the existence of a correlation between the participation of the 5d orbitals in the metal−ligand bonding and the thermal stabilities of the $Ln(TTB)_2$ species (TTB = η^6-(1,3,5-*t*-Bu)$_3C_6H_3$). The thermal stabilities of the $Ln(TTB)_2$ species correlate qualitatively with the free atom $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion energies for the lanthanides. A similar result is reported by King et al. in the case of dissociation energies of the $Ln(TTB)_2$ species, which also correlate with the free atom $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion energies for the lanthanides. The large core RECPs for the lanthanides, leading to formal Ln^{3+} complexes, are extracted from the $f^{n-1}d^1s^2$ atomic configuration and thus properly describe the participation of the 5d orbitals in the bonding. In a similar way, the large core ECP for the Ce atom is extracted from the $f^{n-2}d^2s^2$ configuration as we have a formal Ce^{4+} ion. The large core RECPs used in this work

TABLE 3: Ln-N Bond Length (Å) of $Ln(NH_2)_3$ Complexes Calculated at Different Levels of Theory

metal	HF	B3PW91	B3LYP	MP2
La	2.34	2.31	2.32	2.32
Ce	2.17	2.16	2.27	2.17
Pr	2.31	2.27	2.29	2.29
Nd	2.29	2.26	2.27	2.27
Pm	2.27	2.24	2.26	2.26
Sm	2.26	2.23	2.24	2.24
Eu	2.48	2.43	2.44	2.45
Gd	2.24	2.21	2.22	2.22
Tb	2.22	2.19	2.20	2.20
Dy	2.21	2.18	2.19	2.19
Ho	2.20	2.17	2.18	2.18
Er	2.18	2.16	2.17	2.17
Tm	2.17	2.15	2.16	2.16
Yb	2.39	2.35	2.36	2.37
Lu	2.15	2.13	2.13	2.14

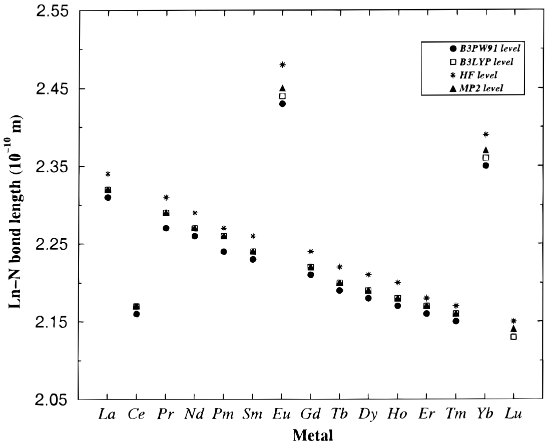

Figure 3. Ln-N bond lengths (Å) for $Ln(NH_2)_3$ complexes at the Hartree-Fock, MP2, B3PW91, and B3LYP level of theory.

describe properly the bonding at lanthanide through, in particular, the participation of the 5d orbitals.

In conclusion to this analysis, it appears that the 4f electrons do not participate in the bonding and that properly chosen large core RECPs can be used to calculate lanthanide complexes. It also appears that DFT or other single reference methods should be usable since open f electrons are only in the core.

Comparison of Levels of Calculation for $Ln(NH_2)_3$. The ground state geometries of all $Ln(NH_2)_3$ complexes were optimized at several levels of theory (HF, MP2, DFT) with large core RECPs. The Ln-N bond lengths are reported in Table 3 and their variation within the lanthanide series is presented in Figure 3. Direct comparison with experimental geometrical parameters is not feasible because of the presence of the silyl groups which could influence the Ln-N distances (see below). Nevertheless, comparing methods should be informative regarding the dependence of the geometry on the level of calculation.

Table 3 shows that all methods lead to similar Ln-N bond lengths and Figure 3 illustrates that all methods give similar results for each atom. As expected, the bond lengths at the HF level are longer by 0.01−0.02 Å than with any other method. This is due to the lack of electronic correlation in the HF calculations when we compare with the DFT or MP2 results. However, the effect of the correlation on the Ln-N bond length is found to be small with respect to that obtained for U−N in the actinide complex UN_2.[36] This is due to the large 5f participation in the case of actinide complex, which adds covalent character to the otherwise strongly ionic bond,[2] resulting in short U−X bonds. The electronic density is, thus, important in the bonding region for the 5f complexes and the correlation effect is high as shown by a decrease of roughly 0.10 Å going from HF to a correlated level. Since the Ln-N bond length vary from 2.30 to 2.13 Å (versus 1.73 Å for U), the effect of the correlation in the bonding region should be drastically reduced. This phenomenom is thus in agreement with the nonparticipation of the 4f atomic orbitals in the chemical bonding in the lanthanide complexes. As shown in Figure 4, the bond angle N−Ln−N along the lanthanide series for the four considered methods shows no variation. Comparison of the correlated methods, namely, DFT (B3PW91 and B3LYP) and MP2, shows that the structural parameters are almost constant. DFT seems, therefore, a method of choice, since it gives the same results as MP2 at a lower computational cost. The two different hybrid functionals B3PW91 and B3LYP give similar results for the Ln-N bond length (Figure 3) or the N−Ln−N bond angle (Figure 4). It has been shown by Parisel et al.[37] that the PW91 correlation functional leads to better results than the LYP correlation functional when a weak interaction, e.g., an agostic interaction, is considered. This suggests that the interactions between Ln and an amido group do not qualify as weak interactions. Our calculations reproduce in a remarkable manner the lanthanide contraction at all levels of calculation. The experimental value of 0.179 Å is quantatively reproduced with B3PW91 and MP2 (0.180 Å), whereas the values are 0.185 Å for HF and 0.190 Å for B3LYP. In all respects, B3PW91 gives the best results and will only be considered hereafter for calculating lanthanide complexes.

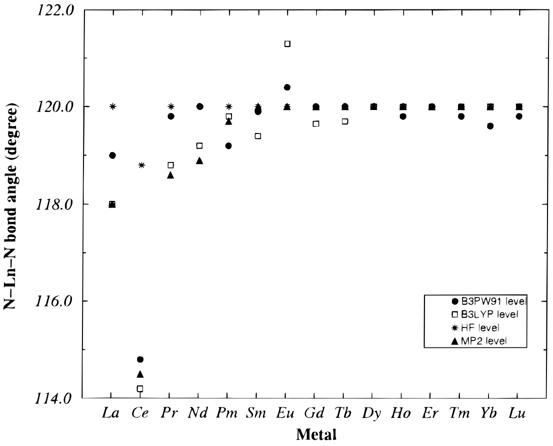

Figure 4. Average N−Ln−N bond angle (degrees) for $Ln(NH_2)_3$ complexes at the Hartree-Fock, MP2, B3PW91, and B3LYP level of theory.

Comparison with a Closer Model to the Real System: Study of $Ln[N(SiH_3)_2]_3$. The trisamidolanthanide complex is known with two trimethylsilyl groups in the amido ligand. We have therefore calculated four representative complexes for La(III), Eu(II), Gd(III), and Lu(III) with SiH_3 as a model of $SiMe_3$. We have used a large core RECP for the lanthanide center and performed DFT calculations with the B3PW91 hybrid functional. For La, Eu, and Lu complexes, the optimized structures show the presence of three β Ln···Si−H agostic interactions, which cannot be present in the experimental trimethylsilylamido system. While this result is interesting on its own standing and will be discussed in a forthcoming paper, we are presently mostly interested in analyzing the most important metal−ligand interaction, i.e., the Ln-N bond. The calculations for Gd show the presence of two minima. The global minimum has three agostic interactions, and the secondary minimum, with only one agostic interaction, is found 11.4 kcal mol^{-1} above. The Gd−N bond length is very close in the two structures (2.27 and 2.24 Å) for the global and the secondary minimum, respectively. The metal−N distance is therefore not very much influenced by the agostic interaction and this allows us to compare the calculated distances for La, Eu, and Lu with the results from diffraction studies. Close agreement is obtained in each case since the experimental and calculated values differ at most by 0.02 Å (La 2.38 Å,calcd 2.40 Å; Eu 2.51 Å, calcd 2.51 Å; Lu 2.18 Å, calcd 2.19 Å). Excellent agreement is also obtained for Si−N bond lengths, which average to 1.70 Å with a deviation of 0.01 Å. This quantitative agreement between solid state structures and calculated models clearly suggests that the method of calculation presented here is very well adapted for the representation of lanthanide complexes.

Conclusions

This work shows that the geometrical parameters of lanthanide complexes can be calculated accurately for any number of f electrons with large core RECPs (f electrons in the core) and within the DFT framework. This is shown to be due to the nonparticipation of f electrons to the Ln−ligand bonding as demonstrated by calculations with small core and large core RECPs. Comparison between DFT and MP2 calculations shows that DFT is the method of choice because it reproduces in a quantitative manner the lanthanide contraction (exptl 0.179 Å vs calcd 0.180 Å) at a reasonable computational cost. In addition to the lanthanide contraction, the absolute Ln-N bond lengths in $Ln[N(SiH_3)_2]_3$ are reproduced with an average deviation of 0.01 Å when compared to the experimental X-ray structures of $Ln[N(SiR_3)_2]_3$. This method of calculation should permit the theoretical investigation of large lanthanide complexes.

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