DFT modeling of ligands in lanthanide chemistry: Is $Ln[N(SiH_3)_2]_3$ a model for $Ln[N(SiMe_3)_2]_3$?

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DFT (B3PW91) calculations with large core ECPs for the whole series $Ln[N(SiH_3)_2]_3$ have been carried out. The calculations find two types of geometries dependant on the silicon basis set. In the absence of d orbitals on Si, the calculations reproduce the helicoidal shape of the molecules and the absence of any agostic interaction. When d orbitals are added to the Si basis set, a corolla structure is obtained as a minimum, in addition to the less stable helicoidal structure. The greater stability of the corolla family is due to the presence of three Ln···Si–H agostic interactions, whose stabilising influence is overestimated by the modeling of $SiMe_3$ by SiH_3 in the vicinity of an electron-deficient lanthanide center. These results suggest that the coordination sphere of the lanthanide center could be highly sensitive to the level of calculation and that great caution should be taken in representing ligands in lanthanide chemistry.

Modeling large substituents and ligands of chemical interest is a necessity and a crucial problem in theoretical chemistry. Models have to be tested and may have to be modified when they lead to unrealistic results. The situation is especially important for transition metal complexes. Ligands like the cyclopentadienyl ion (Cp) have been represented by a chlorine atom with moderate success.[1,2] The modeling of large phosphines by PH_3 has been shown to modify the coordination geometry at the metal.[3,4] For metal centers that are electron deficient, and thus have the potential to coordinate additional ligands, the proper modeling of ligands is of critical importance. In particular, ancillary ligands have been shown to play a leading role in the establishment of agostic interactions.[5,6]

Trivalent lanthanide complexes LnX_3 have a highly unsaturated metal center—consequently, bonding of X to the metal needs to be well modeled and understood. This is especially important in relation to the problem of nuclear wastes. In this sense, theoretical studies of f elements are of increasing interest. Whereas actinide complexes (AnO_2^{2+}; see, for example, ref. 7–9) have been studied, much less is known about lanthanide complexes. Calculations by Dolg and Stoll[10] on small 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.[11] The very limited number of studies[12–15] of lanthanide complexes with open f shells is probably due to the complexity of the DFT calculations in the high-spin configurations. Recently, we[16] have shown the non-participation of the 4f orbitals in the chemical bonding in $Ln(NH_2)_3$ complexes and have proposed a method to calculate this type of complex for the whole series of lanthanide family using large core ECPs on the metal center in combination with DFT calculations. Effective core potentials (ECP) that take into account implicitly the relativistic effects in a Schrödinger or Khon–Sham calculation now make possible computational studies of large systems of chemical interest.

In this paper, we have carried out an investigation of $Ln[N(SiR_3)_2]_3$ for all Ln. This family has been chosen because structures are known experimentally[17–21] for R = Me for a significant number of Ln elements. A trisilylamido ligand would be traditionally represented by $N(SiH_3)_2$. The validity of this model in the case of lanthanide complexes is discussed.

Computational details

The calculations were carried out with the GAUSSIAN 98 suite of programs.[22] The ECPs optimized by the Stuttgart–Dresden group[23–25] were used for lanthanide centers and silicon. Large core ECPs were used according to the method proposed in ref. 16. The large core ECPS were chosen according to the formal oxidation degree of the lanthanide center. Thus, 11 valence electron ECPs were used for the lanthanide(III) centers, 10 valence electron ECPs for the lanthanide(II) (Eu,Yb), leading to negatively charged complexes, and 12 valence electron ECPs for cerium(IV), leading to a positively charged complex. The ECPs were used in combination with their optimized basis sets, which were supplemented by polarization functions, 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 B3PW91[26,27] level of theory was carried out without any symmetry constraint.

Results and discussion

Results without polarization functions on the silicon center

Geometry optimization was carried out for the whole lanthanide series (La to Lu) on $Ln[N(SiN_3)_2]_3$ without including any polarization function on the silicon center. In a previous paper;[16] the Ln–N bond lengths were calculated within the same methodology for the model system $Ln(NH_2)_3$ and Table 1 shows a comparison between these values and the ones obtained for $Ln[N(SiH_3)_2]_3$. As expected, the Ln–N bond lengths are found to be systematically longer (average 0.04 Å) for $Ln[N(SiH_3)_2]_3$ than for $Ln(NH_2)_3$. This is in agreement

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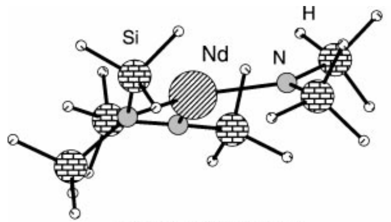
Table 1 DFT(B3PW91) optimized Ln–N bond lengths (Å) for $Ln(NH_2)_3$, $Ln[N(SiH_3)_2]_3$ without a d function on Si and experimental (X-ray) values for $Ln[N(SiMe_3)_2]_3$

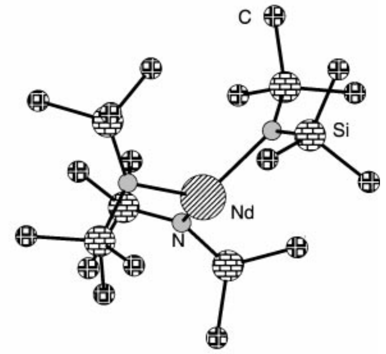
Metal	$Ln(NH_2)_3$ [a]	$Ln[N(SiH_3)_2]_3$ [b]	$Ln[N(SiMe_3)_2]_3$ [c]
La	2.31	2.36	2.40[17]
Ce	2.16	2.21	—
Pr	2.27	2.32	—
Nd	2.26	2.28	2.36[18]
Pm	2.24	2.28	—
Sm	2.23	2.27	—
Eu	2.43	2.48	2.53[19]
Gd	2.21	2.24	—
Tb	2.19	2.23	2.26[20]
Dy	2.18	2.21	2.22[21]
Ho	2.17	2.20	—
Er	2.16	2.19	2.21[18]
Tm	2.15	2.19	—
Yb	2.35	2.39	2.44[19]
Lu	2.13	2.18	2.23[17]

[a] Calculated values from ref. 16. [b] This work. The calculated N–Si bond length is 1.76 Å for all Ln. [c] X-Ray results. The N–Si bond length is 1.70 Å in all cases.

with the common chemical belief that a silicon center strongly stabilizes an α anion and a β cation. The nitrogen p lone pair of the amido group, which makes the π bond with the lanthanide center, is partially delocalized in the SiH_3 group, resulting in a decrease of the Ln–N interaction in $Ln[N(SiH_3)_2]_3$ in comparison to $Ln(NH_2)_3$. The Ln–N and N–Si bond lengths obtained at the DFT(B3PW91) level, along with the available experimental data, are also shown in Table 1. Only the bond lengths have been considered since these parameters are more influenced by the addition of a polarization function on the silicon center than the corresponding (N–Ln–N and Si–N–Si) bond angles. The Ln–N bond lengths are found to be too short and the N–Si bond lengths too long when compared to the experimental values. The two bond lengths differ from the experimental values by around 0.06 Å in the absence of the d function on silicon. However, the overall experimentally observed helicoidal shape of the trimethylsilylamido ligands is well reproduced, as illustrated for the case of the neodymium complex $Nd[N(SiMe_3)_2]_3$ modeled by $Nd[N(SiH_3)_2]_3$ (Fig. 1). The calculation even reproduces, at least qualitatively, the twist of each Si–N–Si plane with respect to the plane containing the three nitrogen atoms. Of note is that the calculations indicate that no β Si–H agostic interaction takes place despite the electron deficit at the metal center. At this stage, SiH_3 seems to be a reasonable model for $SiMe_3$ and the inclusion of a set of polarization functions on the silicon center should just lead to a correction in bond lengths and thus to a representation of $Ln[N(SiH_3)_2]_3$, for any lanthanide center, in even better agreement with experiment.



Helicoidal Structure



Experimental Structure

Fig. 1 DFT(B3PW91) optimised structure (no d function on Si) for $Nd[N(SiH_3)_2]_3$ and experimental (X-ray) structure for $Nd[N(SiMe_3)_2]_3$

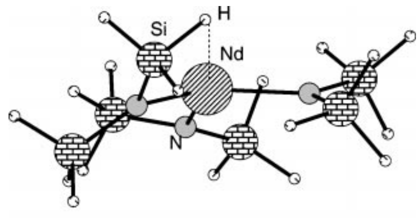
Results with polarization functions on the silicon center

The geometry of the model compound $Ln[N(SiH_3)_2]_3$ for the whole series of lanthanides has been optimized at the DFT(B3PW91) level with a set of polarization functions on the silicon center. Two stable minima on the potential surface of $Ln[N(SiH_3)_2]_3$ have been localized. The bond lengths obtained for the two structures are in excellent agreement with the experimental values (Table 2). The average deviation between the optimized Ln–N bond lengths and the experimental ones is found to be less than 0.02 Å. The optimized N–Si bond length is found to be 1.70 Å, in perfect agreement with the experimental value. Whereas these criteria are very encouraging, examination of the overall shape of the complexes shows the situation to be less satisfactory. Fig. 2 presents the two optimized structures obtained for $Nd[N(SiH_3)_2]_3$. One structure is helicoidal, like that of $Nd[N(SiMe_3)_2]_3$, but exhibits a unique β-agostic Si–H interaction while the experimental structure has none. In contrast, the helicoidal structure does not have any β-agostic interaction in the absence of a d polarization function on Si. The other structure is a corolla, with the silyl groups lying in the plane orthogonal to the one defined by the three nitrogens, and has three β-agostic Si–H interactions. The corolla structure is calculated to be 10 kcal mol^{-1} more stable than the helicoidal minimum for the whole series of lanthanide centers. Comparison between the two structures allows an energy estimate for the agostic Si–H interaction to be made. Previous studies have shown that the bond between Ln and NH_2^- is largely ionic, with little covalent interaction.[16] The SiH_3 substituent further decreases the bonding interaction between Ln and the N centers. For this reason, the rotation around Ln–N is likely to be almost free and the two structures differ essentially by two stabilizing

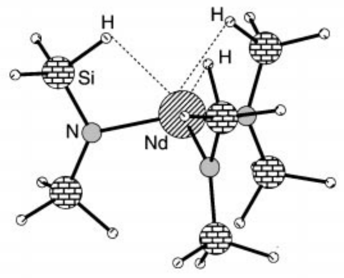
Table 2 DFT(B3PW91) optimized Ln–N bond lengths (Å) for $Ln[N(SiH_3)_2]_3$ with a d polarization function on Si and experimental (X-ray) values for $Ln[N(SiMe_2)_2]_3$[a]

Metal	Exp.	Helicodal	Corolla
La	2.40[17]	2.37	2.39
Ce	—	2.22	2.23
Pr	—	2.33	2.34
Nd	2.36[18]	2.33	2.33
Pm	—	2.31	2.31
Sm	—	2.28	2.29
Eu	2.53[19]	2.50	2.51
Gd	—	2.27	2.27
Tb	2.26[20]	2.25	2.25
Dy	2.22[21]	2.22	2.22
Ho	—	2.22	2.22
Er	2.21[18]	2.21	2.21
Tm	—	2.20	2.21
Yb	2.44[19]	2.41	2.42
Lu	2.23[17]	2.19	2.21

[a] The N–Si bond length is 1.70 Å in all cases, for the X-ray data and both calculated structures.



Helicoidal structure



Corolla Structure

Fig. 2 DFT(B3PW91) helicoidal and corolla structures for $Nd[N(SiH_3)_2]_3$ (d function on Si)

agostic interactions. The strength of the β-agostic interaction can thus be estimated to be around 5 kcal mol^{-1}.

In the present study, the agostic interactions appear to be associated with the inclusion of a set of polarization functions on the silicon center and not only with the electron deficiency of the metal center (see Fig. 1). The set of polarization functions on the silicon centers allows a better description of the delocalization of the nitrogen lone pair to the SiH_3 group leading, as already mentioned, to an excellent description of the Ln–N and N–Si bond lengths (Table 2). The delocalization also involves the hydrogen atoms by making the Si–H bond more electron-rich. The trisilylamido anion is significantly stabilized and the lanthanide center moves out of the plane defined by the three nitrogen atoms, closer to the hydrides, in order to form additional β-agostic Si–H interactions in addition to weak Ln–N bonds. The agostic Si–H interaction is a well-known phenomenon and has been properly reproduced by DFT calculations in transition metal complexes.[28–30]

The present system differs somewhat from other cases. Agostic interactions involve donation from the bond containing the H center to the electron-deficient metal center but also back-donation from the lone pair on the metal into the antibonding orbital of the agostic bond. In the present case, no back-donation is possible, since no d electrons are available. The strength of the agostic interaction is thus closely related to the electronic density in the agostic bond. Mulliken population analysis of the $Nd[N(SiH_3)]_3$ complex illustrates the great importance of the polarization of the d orbitals for accumulating electron density in the Si–H bond. In the helicoidal structure and in the absence of a d function on Si, the charges are $+0.84$ and -0.14 on Si and H. With the d functions on Si, these values become $+0.55$ and -0.10, respectively for the nonagostic SiH_3 group in the helicoidal structure. In the corolla structure, the interaction of the lanthanide center with the Si–H agostic bond results, as expected, in an accumulation of density in the agostic Si–H bond ($+0.55$ for Si and -0.17 for H). The results of the calculations are thus in significant disagreeement with the experimental results. The experimental X-ray crystal structure of $Ln[N(SiMe_3)_2]_3$ does not exhibit any agostic interactions, although it should be kept in mind that the C–H agostic interaction would be weaker than the Si–H one and that the electrons of the Si–C bond are probably not accessible to the metal. In that sense, SiH_3 appears to not be a valid model of $SiMe_3$ for triamidolanthanide complexes since it leads to the formation of interactions that cannot take place in the real complexes.

Conclusion

The calculations of $Ln[N(SiH_3)_2]_3$ to model $Ln[N(SiMe_3)_2]_3$ illustrate some difficulties that may occur in the modeling of chemical systems. The trisilylamido group itself is well represented if the N electrons can delocalize onto the silyl groups. Therefore, as expected, N–Si distances are better reproduced when a d polarization function on Si is included. The coordination around the metal center shows more subtle problems. Earlier calculations on $Ln(NH_2)_3$ as the simplest model for trisamido complexes have reproduced in a satisfactory manner the trigonal planar coordination at the metal center. The distance Ln–N has been found to be slightly too short, which was attributed to the too-strong interaction between the anionic N center and the metal. With the $N(SiH_3)_2$ model, the Ln–N distance increases (and is in excellent agreement with the experimental data) since part of the density of N is moved to the SiH_3 group and is less available for the Ln–N interaction. However, optimal representation of $N(SiH_3)_2$ (with a d function on Si) leads to a large accumulation of electronic density in the Si–H bond, resulting in the occurence of an agostic Ln···Si–H interaction. A structure that cannot occur in the case of the $N(SiMe_3)_2$ group is therefore obtained. Special care should thus be taken in modeling ligands in lanthanide complexes to avoid non-existent interactions between the electron-deficient center and artificially electron-rich part of the ligands. These results also illustrate the need for the lanthanide center to be surrounded by electron-rich ligands.

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