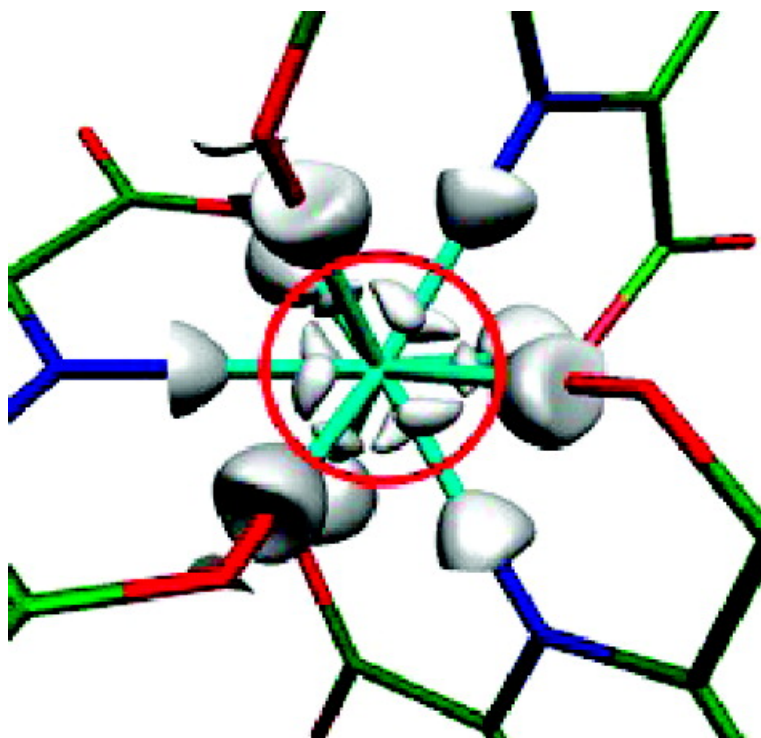


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On the Sensitivity of f Electrons to Their Chemical Environment

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Abstract: Density functional calculations have been carried out on three families of lanthanide complexes of D_3 or C_4 symmetry, namely $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Ln}(\text{DPA})_3]^{3-}$, and $[\text{Ln}(\text{DOTAM})]^{3+}$ ($\text{Ln} = \text{Y}, \text{La}, \text{Lu}$; DPA = pyridine-2,6-dicarboxylate; DOTAM = 1,4,7,10-tetracarbamoylmethyl-1,4,7,10-tetraazacyclododecane), to get some insights concerning the sensitivity of 4f electrons to the surrounding ligands. We show that the electron density accumulations found within 0.7 Å of the metal center, that precisely give the opposite image of the coordination sphere as they are located trans with respect to the Ln-ligand bonds, are almost exclusively due the f electrons. This polarization of the 4f electrons in lanthanides complexes has therefore to be considered as a general feature that plays a crucial role in some experimentally observed phenomena such as the dependency of quadratic hyperpolarizability to the number of f electrons in $[\text{Ln}(\text{DPA})_3]^{3-}$ complexes that we have evidenced.

Introduction

Owing to their very special chemical and physical properties, lanthanides are currently a fascinating and multidisciplinary area of research with applications of growing importance as MRI contrast agent, in bio-imaging/sensing, or in catalysis for example.¹ This tremendous interest triggered the rapid development of a very rich organometallic and coordination chemistry. From a synthetic point of view, lanthanides are considered as hard Lewis acid with 4f electrons shielded from the external perturbations by the 5d and 6s shells, not involved in the chemical bonding.² Therefore, metal–ligand interactions are mainly electrostatic and the complex stability is generally correlated to the stereoelectronic properties of the polydentate or macrocyclic ligands, resulting in a large variety of coordination numbers (3–12) and in the absence of predetermined chemical bonds directionality.^{2b} However, this generally admitted insensitivity of f electrons to their environment is a rough approximation since it is well-known that the spectroscopic properties (absorption, emission, NMR) arising from f electrons are dependent on the local symmetry of the coordination sphere.

As an example, about 10 years ago, Horrocks reported that the europium(III) ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$ absorption transition energies are slightly sensitive to the nature of the surrounding ligands, a variation tentatively assigned to the ligand nephelauxetic effect.³ More recently, Parker showed that modification of the coordination sphere of macrocyclic Eu(III) or Yb(III) complexes by replacement of the axial water ligand by Lewis bases,^{4a} aminoacids,^{4b} or oxy-anions^{4c,d} result in significant variations of the emission bands relative intensity and splitting.^{4c} These chemical modifications also induced changes in the anisotropy of the magnetic susceptibility tensor χ which manifests itself by a displacement of the ${}^1\text{H}$ NMR signals (paramagnetic pseudo-contact term), that can be rationalized by means of Bleaney's theory of magnetic anisotropy,^{5a} and highlighted more recently by Parker et al.^{4a,5b,c}

The theoretical description of these elements remains a matter of debate. On one hand, because of the limited radial extension of 4f orbitals in lanthanides as compared to the 5d and 6s shells, it is of common wisdom to incorporate the f orbitals in the "insensitive" core shell when carrying theoretical studies on

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[‡] Université de Lyon, Ecole Nationale Supérieure de Lyon.

(1) For a general overview see: Kagan, H. *Chem. Rev.* (special issue) **2002**, *102*, 1806–1807.

(2) (a) Cotton, S. A. *C. R. Chim.* **2005**, *8*, 129–145. (b) Kaltsoyannis, N.; Scott, P. In *The f elements*; Oxford University Press: Oxford, 1999. (c) Cotton S. In *Comprehensive Coordination Chemistry II*; Elsevier: Amsterdam, The Netherlands, 1994; Vol. 3, p 93–188 (hardbound).

(3) Frey, S. T.; Horrocks, W. D. J. *Inorg. Chim. Acta* **1995**, 383–390.

(4) (a) Dickins, R. S.; Parker, D.; Bruce, J. I.; Tozer, D. J. *Dalton Trans.* **2003**, 1264–1271. (b) Dickins, R. S.; Aime, S.; Batsanov, A. S.; Beeby, A.; Botta, M.; Bruce, J.; Howard, J. A. K.; Love, C. S.; Parker, D.; Peacock, R. D.; Puschmann, H. *J. Am. Chem. Soc.* **2002**, *124*, 12697–12705. (c) Bruce, J. I.; Dickins, R. S.; Govenlock, L. J.; Gunnlaugsson, T.; Lopinski, S.; Lowe, M. P.; Parker, D.; Peacock, R. D.; Perry, J. J. B.; Aime, S.; Botta, M. *J. Am. Chem. Soc.* **2000**, *122*, 9674–9684. (d) Bretonniere, Y.; Cann, M. J.; Parker, D.; Slater, R. *Chem. Commun.* **2002**, 1930–1931. (e) Parker, D. *Chem. Soc. Rev.* **2004**, *33*, 156–165.

(5) (a) Bleaney, B. J. *Magn. Reson.* **1972**, *8*, 91–100. (b) Bruce, J. I.; Parker, D.; Tozer, D. J. *Chem. Commun.* **2001**, 2250–2251. (c) Di Bari, L.; Pintacuda, G.; Salvadori, P.; Dickins, R. S.; Parker, D. *J. Am. Chem. Soc.* **2000**, *122*, 9257–9264.

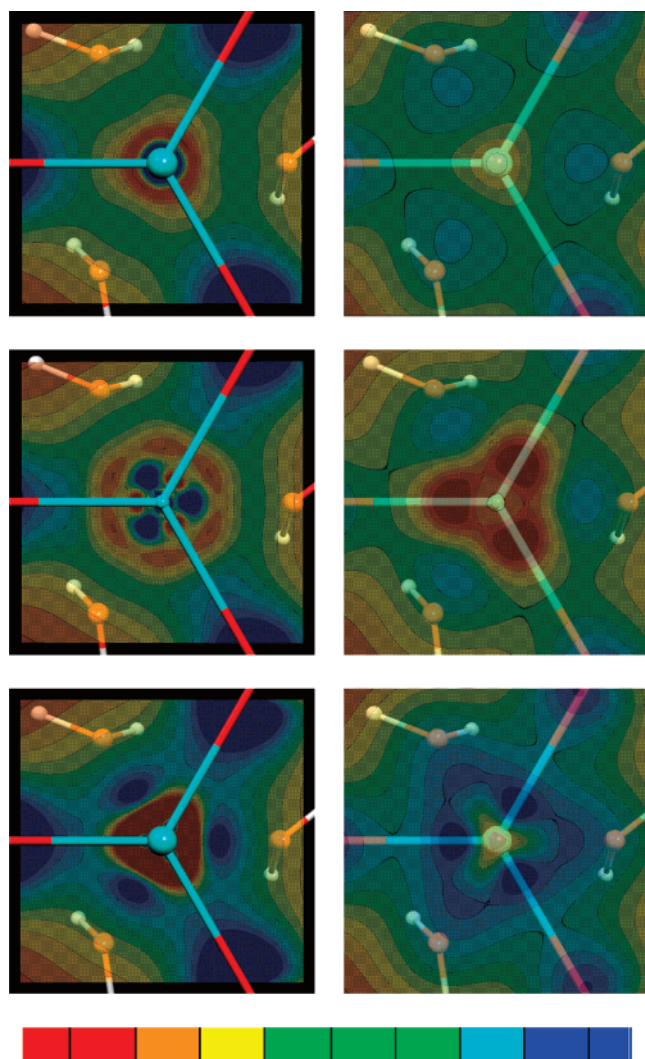
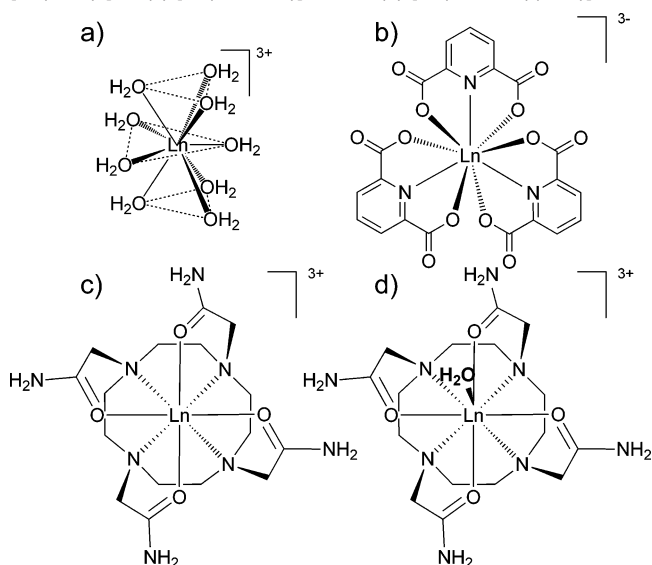


Figure 1. Theoretical deformation density maps calculated for $[Y(H_2O)_9]^{3+}$ (top), $[La(H_2O)_9]^{3+}$ (middle), and $[Lu(H_2O)_9]^{3+}$ (bottom). Maps on the left-hand side column are located in the equatorial plane, while those on the right-hand side are computed $+0.5 \text{ \AA}$ above. M–O bonds outside the equatorial plane are omitted for clarity purpose. For all systems, the color scale ranges from 0 (red) to $+0.01 \text{ e}^-/a_0^3$ (blue).

lanthanide complexes. This approximation reduces the computational effort while giving rise to very satisfactory results as far as structures and bonding are concerned.^{6,7} Recently however, several investigations have pointed out that the generally accepted assumption concerning the nonparticipation of 4f electrons to chemical bonds had to be reconsidered in some peculiar cases, like for the study of the reactivity.^{8–10}

During our ongoing researches in the emerging field of lanthanide complexes for nonlinear optics (NLO), we have

Scheme 1. Molecular Structure of (a) $[Ln(H_2O)_9]^{3+}$, (b) $[Ln(DPA)_3]^{3-}$, (c) $[Ln(DOTAM)]^{3+}$, and (d) $[Ln(DOTAM)(H_2O)]^{3+}$



studied the second-order NLO activity of dipolar $LLn(NO_3)_3$ and octupolar $[Ln(DPA)_3]^{3-}$ complexes ($L =$ dibutylaminophenyl functionalized terpyridine, DPA = pyridine-2,6-dicarboxylate).¹¹ For both cases, we evidenced a direct contribution of the 4f shell filling to the quadratic hyperpolarizability. These unprecedented results clearly indicate that f electrons are sensitive to the external laser electric field, in other words that they are polarizable. The polarizable nature of f electrons had already been suggested in the late eighties, where Chatterjee noted on the basis of X-ray diffraction investigations on the $[Ln(H_2O)_9][CF_3SO_3]_3$ complexes series that the residual electron density maps exhibited nine maxima of approximate D_3 symmetry within 0.7 \AA of the nucleus, these features being moreover strengthened with increasing lanthanoid atomic number.¹² With these two results in hand, we decided to revisit the nature of f electrons by means of density functional calculations. Here, we report a theoretical study describing the influence of the coordination sphere (nature of the ligands and geometries) on f electron density in lanthanide complexes.

Results and Discussion

Deformation electron density maps have been computed by subtracting to the lanthanide complex molecular density, two fragment densities corresponding to the Ln^{3+} relaxed ion on the one hand and to the entire ligand shell kept at their optimized geometries in the complex on the other hand. The resulting density map illustrates the electronic reorganization upon interaction between the metal atom and the ligands. Positive values correspond to electron accumulation. Data concerning the calculations parameters are given in the Computational Details section.

This procedure was first applied to the DFT optimized geometries (see Supporting Information) of the nona-aquo

- (6) For review articles see: (a) Perrin, L.; Maron, L.; Eisenstein, O. *Faraday Discuss.* **2003**, *124*, 25–39. (b) Eisenstein, O.; Maron, L. *J. Organomet. Chem.* **2002**, *647*, 190–197.
- (7) For selected examples see: (a) Dolg, M.; Stoll, H. In *Handbooks of the Physics and Chemistry of Rare Earths*; Elsevier Science: Amsterdam, 1996, Vol. 22, p 607–729. (b) Maron, L.; Eisenstein, O. *J. Phys. Chem. A* **2000**, *104*, 7140–7143. (c) Villa, A.; Cosentino, U.; Pitea, D.; Moro, G.; Maiocchi, A. *J. Chem. Phys. A* **2000**, *3421*–3429. (d) Joubert, L.; Silvi, B.; Picard, G. *Theo. Chem. Acc.* **2000**, *104*, 109–115.
- (8) Schinzel, S.; Bindl, M.; Visseaux, M.; Chermette, H. *J. Phys. Chem. A* **2006**, *11324*–11331.
- (9) Clark, D. L.; Gordon, J. C.; Hay, P. J.; Poli, R. *Organometallics* **2005**, *24*, 5747–5758.
- (10) Clavaguéra, C.; Dognon, J.-P.; Pyykkö, P. *Chem. Phys. Lett.* **2006**, *429*, 8–12.

- (11) (a) Senechal, K.; Toupet, L.; Ledoux, I.; Zyss, J.; Le Bozec, H.; Maury, O. *Chem. Commun.* **2004**, 2180–2181. (b) Senechal-David, K.; Hemeryck, A.; Tancrez, N.; Toupet, L.; Williams, J. A. G.; Ledoux, I.; Zyss, J.; Boucekkine, A.; Guegan, J.-P.; Le Bozec, H.; Maury, O. *J. Am. Chem. Soc.* **2006**, *128*, 12243–12255. (c) Tancrez, N.; Feuvrie, C.; Ledoux, I.; Zyss, J.; Toupet, L.; Le Bozec, H.; Maury, O. *J. Am. Chem. Soc.* **2005**, *13474*–13475.
- (12) (a) Chatterjee, A.; Malsen, E. N.; Watson, K. *Acta Cryst.* **1988**, *B44*, 386–395. (b) Chatterjee, A.; Malsen, E. N.; Watson, K. *Acta Cryst.* **1988**, *B44*, 381–384.

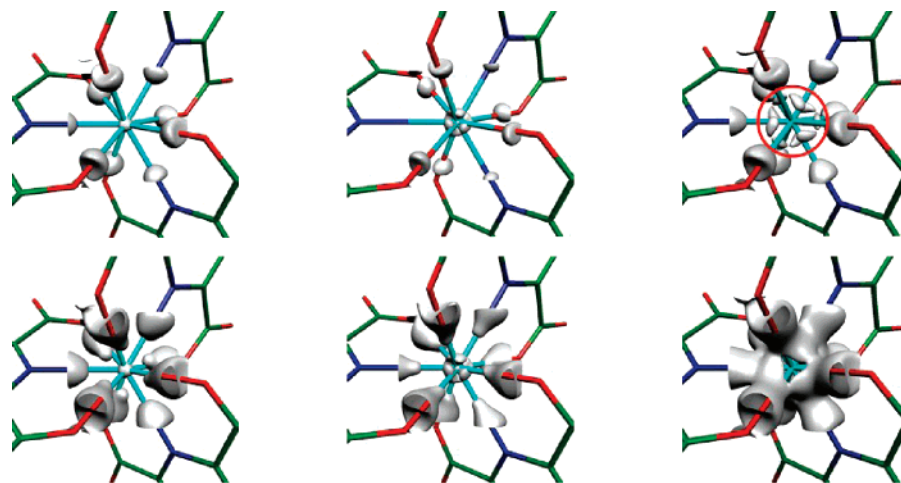


Figure 2. $[\text{Ln}(\text{DPA})_3]^{3-}$ geometries represented together with positive deformation density isosurfaces: Ln = Y (left), La (middle), and Lu (right). Cutoff values: $+0.012 \text{ e}^-/\text{a}_0^3$ (top), $+0.009 \text{ e}^-/\text{a}_0^3$ (bottom). View along the C_3 symmetry axis.

lanthanides $[\text{Y}(\text{H}_2\text{O})_9]^{3+}$, $[\text{La}(\text{H}_2\text{O})_9]^{3+}$, and $[\text{Lu}(\text{H}_2\text{O})_9]^{3+}$. The deformation electron density maps are given in Figures 1 and S1. For $[\text{Lu}(\text{H}_2\text{O})_9]^{3+}$, nine maxima can be found within $\sim 0.6 \text{ \AA}$ of the rare-earth nucleus; each of them being located in trans position with respect to the Lu–O bonds. As such, these density excesses give the opposite image of the ligand sphere, as they are indeed organized in a D_3 symmetric tricapped trigonal prismatic geometry (Scheme 1a). It should be pointed out that the equatorial bonds corresponding to the longest Lu–O distances lead to the three equivalent smallest isovalue lobes. Such features are not present in the calculated deformation maps of two isostructural complexes, namely $[\text{Y}(\text{H}_2\text{O})_9]^{3+}$ and $[\text{La}(\text{H}_2\text{O})_9]^{3+}$, that do not possess f electrons. These findings are in agreement with the main conclusions of Chatterjee et al., described above.¹² It should be pointed out that the electronic depletion zone is not as well clearly structured and is found closer to the metal atom than the density accumulation maxima (see negative deformation electron density maps and isosurfaces given in Supporting information). This results from the fact that the spherical density of the reference Ln^{3+} ion where the electrons are more tightly bound due to the $3+$ charge is pushed away from the nucleus and distorted by the interactions with the ligands. Finally, it is worth pointing out that the previously observed density excesses are missing when performing a test calculation considering 4f orbitals as part of the frozen core, giving therefore further support to our conclusions concerning the polarizability of f electrons in lanthanides.

To examine only the influence of electrostatic interactions and get rid of covalency due to the ligands, we have carried out calculations with a purely electrostatic model where the Ln^{3+} metal ion is only surrounded by nine negative point charges (labeled Q), arranged in a D_3 symmetric tricapped trigonal prism fashion, mimicking the water ligands present in the nona-aquo complexes. A structuration of the deformation density in the vicinity of the Lu(III) rare-earth ion is observed that qualitatively mimics the one found previously, showing that electrons are indeed expelled in the opposite direction to the charges. Upon closer inspection of the linear combination of the valence atomic orbitals, only a small participation of the 5d and 6s shells, which are initially empty in the free ion, is calculated. Indeed, we obtain less than 1% of 5d/6s character in the orbitals derived

from the 4f block. This induces a degeneracy splitting of 0.13 eV of the latter. These results support the conclusions that the 4f electrons are mainly involved in the corresponding density maxima and that the origin of this deformation possesses a significant electrostatic contribution.

In the first molecular series investigated, the rare-earth is only surrounded by oxygen atoms leading to a roughly homogeneous chemical environment. Calculations were also performed on another series of octupolar lanthanides complexes of D_3 symmetry, $[\text{Ln}(\text{DPA})_3]^{3-}$ (Ln = Y, La, Lu) which were recently investigated for their NLO properties (Scheme 1b).^{11c} These complexes offer the opportunity to enlarge the scope of the present study as the nature of the atoms bonded to the lanthanide inside and outside the equatorial plane is different. Examination of the corresponding deformation electron density maps shows that they are consistent with our previous computational results. Indeed, nine density accumulations are found with lutetium as metal atom as shown in Figure 2, while no such features were noticeable in $[\text{Y}(\text{DPA})_3]^{3-}$ and $[\text{La}(\text{DPA})_3]^{3-}$ maps.

It may be argued that the D_3 symmetry would be a prerequisite to observe the given deformation density, as an octupolar expansion may be invoked to explain such features based on the intrinsic properties of f orbitals.¹² To this end, calculations were carried out on a series of $[\text{Ln}(\text{DOTAM})]^{3+}$ complexes (Ln = Y, La, Lu; DOTAM = 1,4,7,10-tetracarbamoylmethyl-1,4,7,10-tetraazacyclododecane) of C_4 symmetry, exhibiting a square antiprism arrangement of the oxygen and nitrogen atoms bonded to the metal ion (see Scheme 1c).¹³ Additionally, the monocapped square antiprism (C_2 symmetry) $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$ complex was also investigated, the oxygen atom of the supplementary water molecule being indeed located along the C_2 axis, on one of the two square faces (Scheme 1d). For all calculations, the same diastereoisomer was considered. The optimized geometries are in good agreement with known X-ray experimental structures.¹⁴ The largest deviation in the Lu–O and Lu–N distances is equal to of 0.04 Å.

(13) DOTAM lanthanide complexes are present under two diastereoisomeric forms, the square antiprismatic being the predominant one. See ref 4a and references therein.

(14) Aime, S.; Barge, A.; Batsanov, A. S.; Botta, M.; Castelli, D. D.; Fedeli, F.; Mortillaro, A.; Parker, D.; Puschmann, H. *Chem. Commun.* **2002**, 1120–1121.

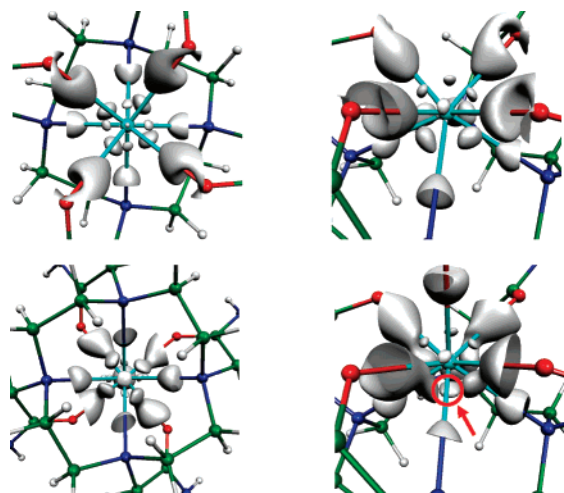


Figure 3. $[\text{Lu}(\text{DOTAM})]^{3+}$ (top) and $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$ (bottom) optimized structures represented together with deformation density isosurfaces. Cutoff values are equal to $+0.013 \text{ e}/a_0^3$ and $+0.011 \text{ e}/a_0^3$ for $[\text{Lu}(\text{DOTAM})]^{3+}$ and $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$, respectively. The two left-hand side pictures correspond to views along the C_n symmetry axis $[\text{Lu}(\text{DOTAM})]^{3+}$, top view; $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$, bottom view.

The angles are perfectly well-reproduced with a difference of less than 1° . The optimized Lu–O(H)₂ bond length is really close to the experimental one (2.404 vs 2.426 Å). It has to be noted that the use of a larger basis set (QZ4P = all electron calculation, four Slater-type orbitals to describe each atomic orbital +4 polarization function) does not improve significantly the geometrical parameters (See Table S2c). Only the lutetium complexes will be discussed, the deformation density maps of yttrium and lanthanum analogous being almost featureless for the selected isosurface criterion, as it might now be expected. In the nonhydrated complex, eight maxima are found (Figure 3), while for hydrated $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$, in a coherent way, an additional density accumulation is clearly present, trans to the Lu–O_w bond (O_w belong to water). Interestingly enough, the size of the isosurfaces follows the trend of the Lu–O/N bond lengths, that is, the shorter the distance, the larger the volume enclosed by the isosurface for a given criterion: for $[\text{Lu}(\text{DOTAM})]^{3+}$, Lu–O and Lu–N bond lengths were estimated to 2.28 and 2.56 Å, respectively, leading to the largest lobe trans to the Ln–O vector. The same observation can be made in the case of the monohydrated complex, where the bond distances are equal to 2.32, 2.42, and 2.65 Å for Lu–O_{DOTA}, Lu–O_w, and Lu–N, respectively.¹⁵ This result unambiguously indicates that the 4f electrons deformation is not restricted to threefold symmetry and reproduces exactly the opposite image of the coordination sphere.

Conclusion

We have demonstrated in this article that the 4f electron density is very sensitive to the coordination sphere: the metal–ligand interaction induces the polarization of 4f density, resulting in the creation of maxima located in trans position to the metal–

ligand bonds. We have shown that the electrostatic contribution to these deformations is significant, and that the positions as well as the magnitude of these maxima are intimately correlated to (i) the nature of the ligands, (ii) their distances to the metal, and (iii) the symmetry of the coordination sphere. Further studies are currently undertaken to corroborate the calculations by experimental measurements using high-resolution X-ray diffraction analysis and to examine the consequences of 4f electron polarization on spectroscopic measurements (absorption, emission or NMR).

Computational Details

Density functional theory calculations were carried out using the Amsterdam density functional (ADF) program developed by Baerends and co-workers.^{16,17} Electron correlation was treated within the local density approximation.¹⁸ The nonlocal corrections of Becke and Perdew were added to the exchange and correlation energies, respectively.^{19,20} The atom electronic configurations were described by a triple- ζ Slater-type orbital (STO) basis set for H 1s and for 2s and 2p of C, N, and O augmented with 2p single- ζ polarization functions for H atoms, and with 3d single- ζ polarization functions for C, N, and O. The atomic basis set of the lanthanide atoms is the following: a triple- ζ STO for the outer 4f, 5d, and 6s orbitals; a double- ζ STO was used for the outer 5p Ln orbitals, 6p polarization functions; a frozen core approximation for the shells of lower energy. Geometry optimizations were carried out using the analytical gradient method implemented by Versluis and Ziegler.²¹ Relativistic corrections were taken into account using the ZORA (zeroth-order regular approximation) scalar Hamiltonian.^{22–24} Representations of the total electronic densities were done using MOLEKEL4.1 program.²⁵

The Cartesian coordinates of the optimized geometries can be found in Supporting Information (Table S1).

Acknowledgment. The authors are grateful to the French Agence Nationale de la Recherche (ANR LnOnL NT05-3_42676) for financial support. The authors also would like to thank Hubert Le Bozec, Guido Pintacuda, and Régis Réau for fruitful discussions.

Supporting Information Available: Deformation density isosurfaces for $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$; Ln = Y, La, Lu and $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$; optimized cartesian coordinates and calculated relative energies of $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Ln}(\text{DPA})_3]^{3-}$, $[\text{Ln}(\text{DOTAM})]^{3+}$, Ln = Y, La, Lu and $[\text{Lu}(\text{DOTAM})(\text{H}_2\text{O})]^{3+}$; selected structural parameters of $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Ln}(\text{DPA})_3]^{3-}$, $[\text{La}(\text{DOTAM})]^{3+}$ and derivatives taken from the TZP or QZ4P calculations and from experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Calculations were also performed for $[\text{Ln}(\text{Q})_4]^{3+}$ in T_d symmetry, and $[\text{Ln}(\text{Q})_4]^{3+}$ in C_4 symmetry. The electronic deformations obtained present four lobes of electronic concentration opposite to the Ln–Q segments. We can unambiguously attribute polarization capability to f electrons of lanthanoid to an external electric potential.

(16) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theo. Chem. Acc.* **1998**, *99*, 391–403.
 (17) te Velde, G.; Bickelhaupt, F. M.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.
 (18) Vosko, S. D.; Wilk, L.; Nusair, M. *Can. J. Chem.* **1990**, *58*, 1200–1211.
 (19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
 (20) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.
 (21) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322–328.
 (22) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597–4610.
 (23) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783–9792.
 (24) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281–293.
 (25) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J.; Swiss Center for Scientific Computing; Manno, 2002.