

$\text{Ln}^{3+}(\text{NO}_3^-)_n$ complexes studied using *ab-initio* quantum chemical calculations

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52

Summary

The structures and interaction energies of $\text{Ln}^{3+}(\text{NO}_3^-)_n$ complexes have been studied using *ab initio* Hartree-Fock method for La^{3+} , Eu^{3+} and Lu^{3+} cations with one to three nitrates in gas phase. The interaction energy between one cation and one bidentate nitrate is 20 to 30 kcal/mol greater than that with one monodentate nitrate. This value is quite lower than the interaction between a cation and one water molecule (about 90 kcal/mol), which could come and complete the hydration sphere of the cation when nitrate's coordination-type moves from bidentate to monodentate. The first studies on these systems with five water molecules in the hydration sphere show changes in the coordination type of nitrates or moves of water molecules in the second sphere.

Introduction and methods

To date, although experimental data give very good measures of bonding distances and cation's coordination number in trivalent lanthanide cations nitrate salts in solid phase, it is difficult to establish the chemical bonding nature (monodentate or bidentate) of nitrate counter-ions in liquid phase. Moreover, in aqueous solution, it is important to assess the competition between trivalent cations and nitrate and between trivalent cations and solvent molecules. Our poster presents a theoretical study on the characterization of $\text{Ln}^{\text{III}}(\text{NO}_3^-)$ complexes using quantum mechanics methods, in order to give some new information about these questions.

Ab initio calculations were done using Gaussian 98 program's Hartree-Fock method. Two kinds of gaussian functions basis sets were used to describe atoms H, N and O. Geometry optimizations were done using 6-31G* basis sets. Interaction energies were calculated using 6-31+G* basis sets. The 46+4fⁿ core electrons of the lanthanide cations were described by a quasi-relativistic effective core potential (ECP) of Dolg et al. and the valence electrons by a (7s,6p,5d)/[5s,4p,3d] gaussian functions basis set.

1. $\text{Ln}^{\text{III}}(\text{NO}_3^-)_n$ complexes in gas phase

In the following, we first discuss the interaction energies and structural features of the $\text{Ln}^{\text{III}}(\text{NO}_3^-)_n$ complexes in gas phase, for cations La^{3+} , Eu^{3+} and Lu^{3+} , and for 1 to 3 nitrates.

1:1 nitrate complexes present two possible geometries. The nitrate can be monodentate or bidentate to the cation. The Ln^{3+} --O distance between cation and nitrate's coordinated oxygen is 0,25 Å greater in the case of the bidentate complex (La^{3+} --O = 2,30 Å). Interaction energy of monodentate cation / nitrate is also roughly 30 kcal/mol greater than that of the bidentate complex (-426 kcal/mol pour La^{3+}).





Géométrie			Distance Ln ³⁺ - O	Q(Ln ³⁺)	E _{int.} (kcal/mol)
		La ³⁺	2.04	2.84	- 397
		Eu ³⁺	1.95	2.86	- 420
		Lu ³⁺	1.86	2.73	- 445
		La ³⁺	2.30	2.82	- 426
		Eu ³⁺	2.20	2.81	- 452
		Lu ³⁺	2.10	2.71	- 480

Table 1 : Ln³⁺/NO₃⁻ 1:1 complexes. Ln³⁺--O : distance between cation and nitrate's binding oxygen, Q(Ln³⁺) : partial charge of the Ln³⁺ cation, and E_{int.} : interaction energy of the complex (kcal/mol)

Concerning 2:1 nitrate complexes, there are for each cation three possible complexation geometry types, monodentate-monodentate, monodentate-bidentate or bidentate-bidentate. The evolution from monodentate to bidentate type increases the interaction energy by 25 kcal/mol and also the Ln³⁺--O distance by 0,1 to 0,2 Å.

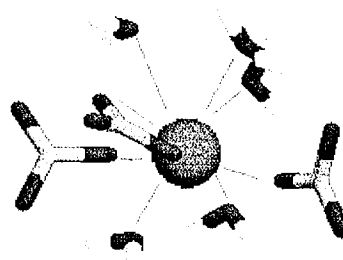
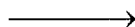
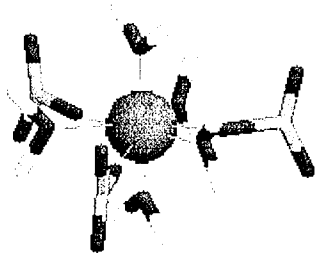
With three nitrates, there are four possible complexation geometry types, according to the nitrate coordination. For the three-bidentate type complex (coordination number CN = 6), Ln³⁺--O distances are 0,1 Å shorter than X-Ray diffraction data (La³⁺: 2,6 - 2,7 Å; Lu³⁺: 2,4 - 2,5 Å). The passage from monodentate to bidentate type increases the Ln³⁺--O distances by 0,2 to 0,3 Å. Increase of interaction energy (20 kcal/mol) is lower than in the case of one and two nitrate complexes. This increase is much smaller than the interaction energy between a trivalent cation and a water molecule (~ 90 kcal/mol). That means, for a constant coordination number, a "bidentate nitrate / cation" complex is less favorable, according to energy, than a "monodentate nitrate / 1 water molecule / cation".

For all coordination type complexes, from La³⁺ to Lu³⁺, the Ln³⁺--O distances decreases according to the lanthanide contraction. The cation's electronic charge decreases (that means the charge transfer increases), and interaction energy increases. These variations increase with the augmentation of the cation's coordination number CN.

2. First hydration sphere of Ln^{III}(NO₃)_n complexes in gas phase

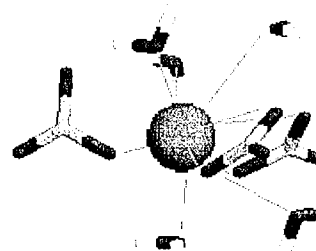
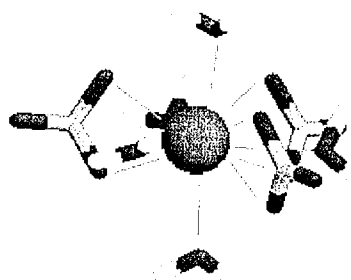
In a second step, in the case of three nitrate La³⁺ and Lu³⁺ complexes, cation's coordination sphere was filled with five water molecules. Thus, the starting values of CN are lower (8) or upper (11) than experimental values (9 to 10 according to the cation). When the starting CN value is lower, the optimized geometry get it increased to 9 for both cations. When the starting value is 11, it becomes 10 for La³⁺ and 9 for Lu³⁺ (nitrate's coordination type is modified). In this last case, in the Lu³⁺ complex, a water molecule is transferred to the second coordination sphere of the cation.

Start: 3 monodentate $\text{NO}_3^- + 5 \text{H}_2\text{O}$. La^{3+} , Lu^{3+} . CN = 8

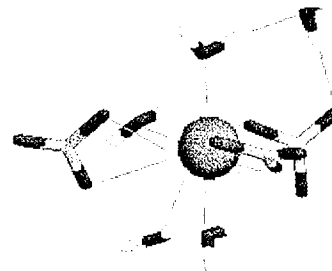


La^{3+} , Lu^{3+} . CN = 9

Start: 3 bidentate $\text{NO}_3^- + 5 \text{H}_2\text{O}$. La^{3+} , Lu^{3+} . CN = 11



La^{3+} , CN = 10



Lu^{3+} , CN = 9

Table 2: Geometry optimization of the first hydration sphere of La^{3+} and Lu^{3+} complexes with nitrate ions. Starting (left) and final (right) structures of the complexes.

Conclusions

This quantum chemical study shows new results both in energetic and geometric investigations of such $\text{Ln}^{3+}(\text{NO}_3^-)_n$ complexes in the gas phase. The differences of interaction energy, due to the change from monodentate to bidentate coordination of nitrate ions in these complexes, are much less than the interaction energy value between the trivalent cations and a water molecule. The geometry conformation "1 monodentate nitrate / 1 water molecule / 1 cation" should be to the advantage of "1 bidentate nitrate / 1 cation" complex configuration in aqueous solution. The first studies in the complete coordination sphere of the cations, fulfilled with water molecules, show the two kinds mono- and bidentate coordination type for nitrates in the same complex.

The continuation of this study will concern a precise characterization of $\text{Ln}^{3+}(\text{NO}_3^-)_3(\text{H}_2\text{O})_n$ complexes in the gas phase (using quantum chemical calculations) or on the $\text{Ln}^{3+}(\text{NO}_3^-)_3$ complexes in the aqueous solution (using molecular dynamics calculations).