Interaction of trivalent lanthanide cations with nitrate anions: a quantum chemical investigation of monodentate/bidentate binding modes†

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We report *ab initio* quantum mechanical calculations on $Ln^{III}(NO_3^-)_n$ (n = 1–3) and $Ln(NO_3)_3(H_2O)_m$ (m = 4–6) complexes to compare the monodentate *vs.* bidentate binding mode of nitrate anions to trivalent lanthanide cations (La^{III}, Eu^{III} and Lu^{III}) in the gas phase. In all $Ln^{III}(NO_3^-)_n$ complexes studied, bidentate coordination is preferred (by about 30 kcal mol^{-1} for $n = 1$ and 20 kcal mol^{-1} for $n = 3$). In the $Ln(NO_3)_3(H_2O)_m$ aggregates, however, where the first coordination shell is saturated, the two types of binding modes become of similar energy, leading to different coordination numbers (CNs) and distributions of first and second shell water molecules. For instance, for $La(NO_3)_3(H_2O)_6$, CN ranges from 9 (3 monodentate nitrates + 6 water) to 10 (3 bidentate nitrates + 4 water) or 11 (3 bidentate nitrates + 5 water). Thus, at some point, adding water to the second or to the first shell becomes isoenergetic. As the cation becomes smaller, the preference for monodentate nitrate binding increases, due to avoided repulsions in the first coordination sphere. Thus, water coordination to the lanthanide cations may induce a change of anion coordination mode and of coordination number. The fact that in solid state structures bidentate binding is dominant thus does not result from a marked intrinsic preference.

There is much interest in the coordination chemistry of lanthanide cations, in relation to important processes such as ion extraction and separation[1,2] or the design of photoactive systems.[3,4] In condensed phases, the composition and structure of their first coordination shell depends on the nature and concentrations of counterions and of other ligands, including solvent molecules. In this paper, we focus on nitrate salts of lanthanides, as these cations are generally extracted from nitric acid solutions of nuclear wastes. The anion binding mode in concentrated solutions remains unclear, especially in the presence of water. In pure aqueous solution, lanthanide nitrate salts are mostly dissociated at low concentrations[5–7] but in solvent extraction processes, the cations are complexed and extracted with their counterions into a water-saturated organic phase, forming stronger ion pairs. The question of anion binding mode is crucial in relation to the stoichiometry of the extracted complex. For instance, according to molecular dynamics (MD) simulations on $Eu(NO_3)_3(TBP)_n$ (TBP = tri-n-butylphosphate) complexes in water with increasing numbers of ligands, the cation typically coordinates 3 TBP ligands when nitrates are bidentate, and 4 to 5 TBPs when nitrates are monodentate.[8] In addition, simulations with nitrates constrained to be bidentate showed that the first coordination is saturated by the anions and TBP only, and that the resulting complex is hydrophobic. Unconstrained nitrates became monodentate, allowing for additional coordination of two more water molecules. The formed complexes are thus too hydrophilic to be extracted to an organic medium. The question of anion binding mode is thus critical for understanding the hydrophilic *vs.* hydrophobic character of the complex. The monodentate coordination found from MD simulations on lanthanide[8,9] or uranyl[10] complexes in aqueous solution contrasts with the dominant bidentate coordination of nitrates in solid state structures,[11] also taken as a reference for molecular modeling studies.[12] Whether this artefactually results from deficiencies in the representation of the potential energy in the MD simulations or corresponds to a real state is presently unclear. Monodentate coordination allows for coordination of additional ligands (*e.g.*, water molecules), as well as increased hydrogen bonding interactions between the first and second shells. The most satisfactory theoretical approaches to this question require quantum mechanical (QM) methods to account for electronic reorganization (mostly polarization and charge transfer) effects upon ligand coordination to the cation. As a first step, we consider in this paper nitrate complexes, first in the absence of competing species, and then in the presence of competing water molecules.

We report a QM investigation on the structural, electronic and energy features of intrinsic (gas phase) nitrate coordination to lanthanide cations (La^{III}, Eu^{III}, Lu^{III}), with a particular focus on monodentate *vs.* bidentate binding modes in the gas phase. We first consider the $Ln^{III}(NO_3^-)_n$ complexes (n = 1–3) and calculate the corresponding interaction energies. Complexes with up to five[13] or six[14] nitrates do exist, but we restrained our study to three nitrates, which corresponds to charge neutrality of the complex. Our aim is to understand the intrinsic coordination type of nitrate, when the first shell is unsaturated. Then, we consider the neutral $Ln(NO_3)_3(H_2O)_m$ aggregates, with four to six water molecules, again comparing the monodentate *vs.* bidentate binding mode of the anions. In these aggregates the first coordination sphere of the cation is close to saturation or saturated[11] and the anion binding mode results from the competition between the attractions with the

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† Electronic supplementary information (ESI) available: table of computed BSSE energies for $La^{III}(NO_3^-)_n$ and $La(NO_3)_3(H_2O)_m$. See http://www.rsc.org/suppdata/nj/b1/b104333c/

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cation and the repulsions within the first coordination sphere. The latter are expected to be larger for bidentate than for monodentate anion binding and for small and hard cations.

Methods

The systems were optimized by QM *ab initio* calculations at the HF level using the GAUSSIAN-94 and GAUSSIAN-98 packages.[15,16] The 46 + 4f^n core electrons of the lanthanide cations were described by the quasi-relativistic effective core potential (ECP) of Dolg *et al.*[17] and the valence electrons by a (7s,6p,5d)/[5s,4p,3d] Gaussian function basis set. All structures were fully optimized using analytical gradients and the 6-31G* basis sets for N, O and H. The optimized structures were recalculated with 6-31+G* basis sets with additional diffuse Gaussian functions at the HF level, as well as using DFT theory with the B3LYP hybrid exchange functional. According to the tests performed by us and others,[18–20] this methodology is sufficient to describe the main energetic and structural characteristics of the lanthanide complexes. The total interaction energy of a given complex was calculated as

$$\Delta E = E[\mathrm{Ln(NO_3)}_n\mathrm{(H_2O)}_m] - E[\mathrm{Ln^{III}}] - nE[\mathrm{NO_3}^-] - mE[\mathrm{H_2O}]$$

with the 6-31+G* basis sets. The basis set superposition error (BSSE) was computed in typical cases using the counterpoise method.[21] For a given number of anions and water molecules the BSSE was found to be nearly constant and independent of the nitrate binding mode and cation size (see ESI).[22] We thus report here the uncorrected ΔE values. The atomic charges were calculated using the Mulliken populations for all systems, as well as using the NBO charge definition for the $\mathrm{Ln^{III}(NO_3^-)}_n$ complexes.

Results and discussion

In the following, we denote the nitrate binding mode "m" for monodentate and "b" for bidentate. Thus, with one nitrate ($n = 1$), complexes are of [m] or [b] type, with two nitrates ($n = 2$), they are of [m,m], [m,b] or [b,b] type, while with three nitrates ($n = 3$), they range from [m,m,m] to [b,b,b]. For a given type, several geometries have also been considered. Since monodentate nitrates became bidentate during the optimization of $\mathrm{Ln^{III}(NO_3^-)}_n$ complexes, we forced them to remain monodentate by constraining the corresponding Ln–O–N angle to be linear. For simplicity, we consider the energies obtained from HF calculations, as the conclusions obtained by DFT calculations are similar.

The QM optimized $\mathrm{Ln^{III}(NO_3^-)}_n$ complexes

The interaction energies and geometries of $\mathrm{Ln^{III}(NO_3^-)}_n$ complexes are given in Table 1. The per anion binding energies are quite large, in line with the high Coulombic attractions, and decrease when the number of anions increases: from 426 to 294 kcal mol^{-1} for La$^{\mathrm{III}}$ bidentate complexes and from 480 to 328 kcal mol^{-1} for bidentate Lu$^{\mathrm{III}}$ complexes. DFT binding energies are somewhat larger than those obtained at the HF level, but yield the same conclusions and trends, as far as the preferred anion binding mode is concerned (Table 1). We thus report HF results only in the following. For all $\mathrm{Ln^{III}(NO_3^-)}_n$ complexes we considered, bidentate coordination is found to be preferred and the interaction energies ΔE follow the cation hardness (La < Eu < Lu). Accordingly, the Ln–O$_{\mathrm{nitrate}}$ bonds shorten from lanthanum to lutetium complexes. Some details are given below.

In the $\mathrm{Ln(NO_3)}^{2+}$ complexes, the [b] coordination mode is preferred to [m] and the difference increases with cation hardness (from 29 kcal mol^{-1} for La$^{\mathrm{III}}$ to 35 kcal mol^{-1} for Lu$^{\mathrm{III}}$). However, the corresponding Ln–O$_{\mathrm{nitrate}}$ bonds are 0.25 Å longer for the [b] than for the [m] nitrates. The cationic Mulliken charge ranges from 2.54 to 2.49 e$^-$ and is smallest with Lu$^{\mathrm{III}}$, which indicates that the electron transfer to the cation is largest in the most stable complex. It is also somewhat larger (by 0.02 e$^-$) for bidentate than for monodentate nitrate, also in line with the reported energy trends. Cation NBO charges, although about 0.2–0.4 e$^-$ more positive than the Mulliken charges, display similar trends.

For the $\mathrm{Ln(NO_3)_2}^+$ complexes, we compared [m,m], [b,m] and [b,b] binding modes and, for each cation, the co-planar, perpendicular and "bent" initial arrangements of the anions (Fig. 1). After optimization, the co-planar and perpendicular arrangements are found to be of similar stability for [m,m] and [b,m] structures. The bent form was somewhat more stable (by about 5 kcal mol^{-1} for La$^{\mathrm{III}}$ and Eu$^{\mathrm{III}}$, and 3 kcal mol^{-1} for Lu$^{\mathrm{III}}$), corresponding to an angle of about 120° between the planes of the anions. Similar "bending" has been reported by Kaupp and Schleyer in mono-, di- and trivalent cation complexes with small ligands.[23] For the [b,b] coordination, the co-planar form is slightly less stable than the perpendicular and bent arrangements for La$^{\mathrm{III}}$ and Eu$^{\mathrm{III}}$. The corresponding [b,b] Lu$^{\mathrm{III}}$ "bent" complex converged to a perpendicular D_{2d} structure, presumably to reduce the anion–anion repulsions, which are largest with the smallest cation and for bidentate nitrates.

Energy differences between co-planar, perpendicular or bent geometries are small, though, compared to those observed upon changing from bidentate to monodentate coordination (about 25 to 32 kcal mol^{-1} from [m,m] to [b,m] and [b,b] complexes). This is 3 to 5 kcal mol^{-1} less than in the $\mathrm{Ln(NO_3)}^{2+}$ complexes with one nitrate. In the cation series, we notice that the interaction energy difference of La$^{\mathrm{III}}$ *vs.* Lu$^{\mathrm{III}}$ is largest in the most stable [b,b] complexes (about 90 kcal mol^{-1}) and weakest in the [m,m] complexes (75 kcal mol^{-1}).

The Ln–O$_{\mathrm{nitrate}}$ bonds are about 0.1 to 0.2 Å longer in $\mathrm{Ln(NO_3)_2}^+$ than in the corresponding $\mathrm{Ln(NO_3)}^{2+}$ complexes, but follow the same trends, also being about 0.2 Å longer for bidentate than for monodentate nitrates (Table 1). The cation charge is also less positive with bidentate than with monodentate anions, and decreases in the order: [m,m] > [b,m] > [b,b] for a given cation, and from La$^{\mathrm{III}}$ to Lu$^{\mathrm{III}}$ in the cation series.

For the neutral $\mathrm{Ln(NO_3)_3}$ complexes, we considered four arrangements: [m,m,m], [b,m,m], [b,b,m] and [b,b,b], starting with the plane of the anions in "vertical" positions. Optimized structures are of approximate D_{3h}, C_{2v}, C_{2v} and D_{3h} symmetry, respectively (see Fig. 2). The per anion energy difference between [m,m,m] and [b,b,b] forms ranges from 19 kcal mol^{-1} for La$^{\mathrm{III}}$ to 22 kcal mol^{-1} for Lu$^{\mathrm{III}}$, which is about 5 kcal mol^{-1} less than in the corresponding $\mathrm{Ln(NO_3)_2}^+$ complexes, but still indicates a marked preference for bidentate

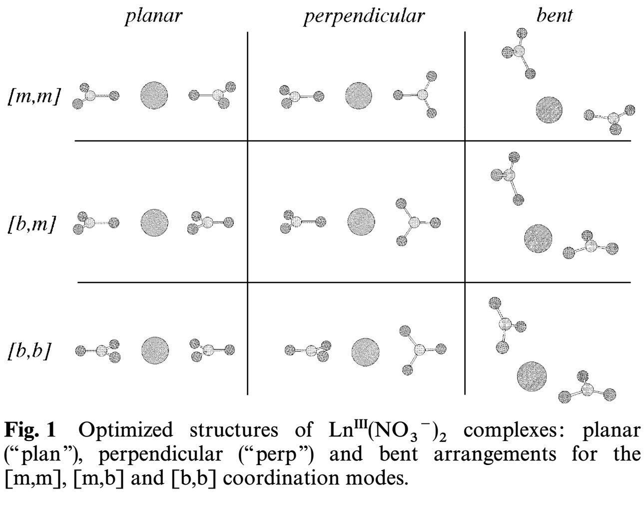


Fig. 1 Optimized structures of $\mathrm{Ln^{III}(NO_3^-)_2}$ complexes: planar ("plan"), perpendicular ("perp") and bent arrangements for the [m,m], [m,b] and [b,b] coordination modes.

Table 1 Characteristics of optimized $Ln^{III}(NO_3^-)_n$ complexes: Ln–O distances, cation NBO and Mulliken charges q(Ln) and interaction energy ΔE

	Geometry[a]	Ln	Ln–$O_{nitrate}$/Å	$q(Ln)_{NBO}$/e^-	$q(Ln)_{Mull}$/e^-	$-\Delta E_{HF}$[b]/kcal mol^{-1}	$-\Delta E_{DFT}$[c]/kcal mol^{-1}
[m]		La	2.04	2.84	2.52	396.9	443.5
		Eu	1.95	2.86	2.51	420.4	469.6
		Lu	1.86	2.73	2.50	444.6	492.7
[b]		La	2.30	2.82	2.54	425.8	458.9
		Eu	2.20	2.81	2.51	451.7	487.3
		Lu	2.10	2.71	2.49	480.1	515.3
[m,m]	Plan	La	2.20	2.86	2.43	649.5	692.9
		Eu	2.10	2.91	2.42	685.4	730.5
		Lu	2.00	2.72	2.42	726.2	769.5
	Perp	La	2.20	2.86	2.43	649.5	693.0
		Eu	2.10	2.91	2.42	686.5	730.7
		Lu	2.00	2.72	2.42	726.2	769.6
	Bent	La	2.15	2.84	2.41	655.2	702.2
		Eu	2.06	2.90	2.40	690.3	739.5
		Lu	1.97	2.66	2.39	729.2	776.2
[b,m]	Plan	La	2.20–2.43	2.82	2.40	675.4	714.7
		Eu	2.10–2.32	2.84	2.37	714.2	754.9
		Lu	2.00–2.21	2.65	2.33	758.5	797.6
	Perp	La	2.20–2.42	2.82	2.40	675.7	715.4
		Eu	2.10–2.32	2.84	2.37	715.6	756.0
		Lu	2.00–2.21	2.65	2.33	758.8	803.8
	Bent	La	2.16–2.40	2.79	2.37	681.1	723.3
		Eu	2.06–2.30	2.82	2.35	718.5	762.9
		Lu	1.96–2.16	2.61	2.33	760.8	802.8
[b,b]	Plan	La	2.41	2.76	2.36	698.8	735.9
		Eu	2.34	2.76	2.31	739.6	776.0
		Lu	2.23	2.59	2.25	786.7	821.3
	Perp	La	2.41	2.76	2.35	704.4	739.2
		Eu	2.32	2.75	2.30	744.0	782.2
		Lu	2.21	2.57	2.25	791.2	827.8
	Bent	La	2.41	2.74	2.33	704.5	742.4
		Eu	2.30	2.73	2.28	744.2	783.6
		Lu	—[d]	—[d]	—[d]	—[d]	—[d]
[m,m,m]		La	2.25	2.84	2.35	825.1	865.0
		Eu	2.15	2.90	2.34	868.2	909.9
		Lu	2.04	2.58	2.33	916.7	956.7
[b,m,m]		La	2.25–2.48	2.78	2.31	845.8	883.6
		Eu	2.15–2.37	2.81	2.28	890.8	930.2
		Lu	2.05–2.26	2.50	2.26	941.4	979.4
[b,b,m]		La	2.26–2.49	2.70	2.26	865.0	900.5
		Eu	2.15–2.38	2.71	2.21	911.4	948.7
		Lu	2.05–2.28	2.43	2.17	963.5	999.5
[b,b,b]		La	2.58	2.62	2.20	882.6	916.5
		Eu	2.39	2.59	2.13	930.0	965.4
		Lu	2.29	2.36	2.07	983.5	1017.1

[a] Planar, perpendicular or bent structures (see Fig. 1). [b] From HF/6-31+G*//HF/6-31G* calculations. [c] From DFT/6-31+G*//HF/6-31G* calculations. [d] Converged to a perpendicular form during the optimization.

binding. The Ln–$O_{nitrate}$ distances are 0.2 to 0.3 Å longer for bidentate than for monodentate coordination. They are also 0.1 to 0.2 Å longer than in the $Ln(NO_3)_2^+$ complexes, in line with the weaker per nitrate binding energy.

The cation Mulliken or NBO charges are about 0.2 e^- less positive in [b,b,b] than in [m,m,m] complexes, confirming the larger electron transfer with bidentate ligands. For a given cation and anion binding mode, this charge decreases with the number of anions (*e.g.*, [m] > [m,m] > [m,m,m] and [b] > [b,b] > [b,b,b]). The electron transfer to the metal is thus largest (0.93 e^-) for the Lu^{III} cation and for three bidentate nitrates.

Concerning the geometry of the complexed nitrate ligands, it is of C_{2v} instead of D_{3h} symmetry. Upon complexation, the N–O_{Ln} bond involving the coordinated oxygen(s) lenghtens (by about 0.2 Å for monodentate and 0.1 Å for bidentate binding), while the "exo" N–O bond(s) shorten(s) (by about 0.01 Å). This follows trends observed in vibrational spectra of complexed nitrates,[24] as well as in X-ray structures.[11]

The QM optimized $Ln(NO_3)_3(H_2O)_m$ aggregates

In this section we focus on the influence of additional ligands (water molecules) on the coordination type of the nitrate ions

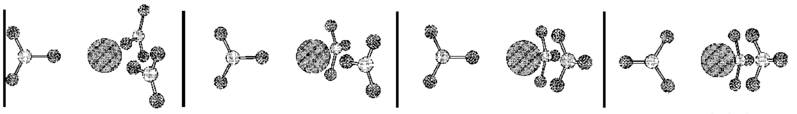

[m,m,m] *[b,m,m]* *[b,b,m]* *[b,b,b]*

Fig. 2 Optimized structures of $Ln^{III}(NO_3^-)_3$ complexes with the [m,m,m] to [b,b,b] coordination modes.

in neutral complexes. We consider $Ln(NO_3)_3(H_2O)_m$ systems, with four to six water molecules and the largest (La^{III}) and smallest (Lu^{III}) cations only. The behaviour of Eu^{III} complexes should be intermediate. The initial structures of these aggregates were first built with $Ln–O_{nitrate}$ and $Ln–O_{water}$ distances of 2.45 Å, adding the water molecules to the first shell of the $Ln(NO_3)_3$ scaffold as indicated below. In some cases, we also considered X-ray structures of lanthanide hydrates where all nitrates are bidentate, as well as models derived from the model-built structures where water molecules are shifted. Geometry optimization was performed without imposing constraints, and in some cases, changes in nitrate coordination mode took place. Some water molecules also moved from the inner to the outer coordination sphere. We denote w1 + w2 (= m) the distribution of first shell (w1) and second shell (w2) water molecules. The main energy and structural results (initial and optimized complexes) are shown in Table 2. The coordinates of the optimized systems can be obtained from the authors.

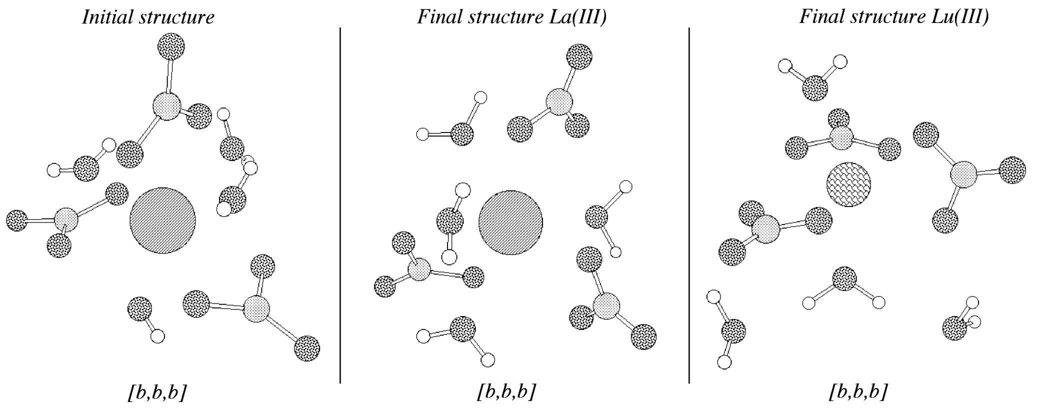
The $Ln(NO_3)_3(H_2O)_4$ complexes. These were built consistently from the optimized [b,b,b] $Ln(NO_3)_3$ complexes, adding the four water molecules at the corners of a tetrahedron centered on the cation (Fig. 3). As nitrates were bidentate, the coordination number was initially 10 for the two cations. The [m,m,m] complexes were not considered, as the corresponding CN of 7 is too low, compared to the usual experimental values.

After minimization, the nitrates are bidentate as in the starting structure (Fig. 3). In the case of the $La(NO_3)_3(H_2O)_4$ complex, the four water molecules remain coordinated to the cation (at 2.6–2.7 Å), leading to a coordination number (CN) of 10. The $La–O_{nitrate}$ distances are about 0.05 Å longer than

Table 2 Characteristics of the optimized $Ln(NO_3)_3(H_2O)_m$ aggregates: nitrate binding mode, metal hydration and coordination number (CN), Ln–O distances, cation Mulliken charge q(Ln) and total interaction energy ΔE (in kcal mol^{-1})

Initial structure	Optimized La^{III} complexes						Optimized Lu^{III} complexes					
Nitrates w1 + w2[a]	Nitrates w1 + w2[a]	CN	$La–O_{nitrates}$/Å	$La–O_{water}$/Å	q(La)/ e^-	$-\Delta E^b$ HF *DFT*	Nitrates w1 + w2[a]	CN	$Lu–O_{nitrates}$/Å	$Lu–O_{water}$/Å	q(Lu)/ e^-	$-\Delta E^b$ HF *DFT*
[b,b,b] 4 + 0	[b,b,b] 4 + 0	10	2.59–2.66	2.64–2.74	2.07	957.5 *978.5*	[b,b,b] 2 + 2	8	2.35–2.37 [b]	2.29–2.39 4.18–4.23[c]	2.00	1055.3 *1083.6*
[b,b,b] 4 + 0							[b,b,m] 4 + 0	9	2.37–2.46 [b] 2.38 [m]	2.36–2.51	2.01	1051.4 *1078.0*
[m,m,m] 5 + 0	[b,m,m] 5 + 0	9	2.62–2.63 [b] 2.50–2.59 [m]	2.58–2.72	2.09	967.5 *990.8*	[b,m,m] 5 + 0	9	2.37–2.47 [b] 2.29–2.32 [m]	2.41–2.52	1.98	1061.5 *1089.1*
[b,b,b] 5 + 0	[b,b,m] 5 + 0	10	2.61–2.65 [b] 2.57 [m]	2.62–2.72	2.09	970.5 *992.9*	[b,b,b] 4 + 1	10	2.40–2.62 [b]	2.42–2.49 4.15[c]	1.96	1064.6 *1091.5*
[b,b,b] 5 + 0	[b,b,m] 5 + 0		2.61–2.65 [b] 2.57 [m]	2.62–2.72	2.02	967.5 *993.1*	[b,b,m] 4 + 1	9	2.37–2.51 [b] 2.37 [m]	2.3–2.5 4.34[c]	1.87	1066.7 *1095.5*
[b,b,b] 4 + 1[d]	[b,b,b] 4 + 1	10	2.58–2.66 [b]	2.62–2.71 4.45[c]	2.02	969.7 *992.9*	[b,b,b] 4 + 1	10	2.37–2.60 [b]	2.33–2.51 4.38[c]	1.89	1063.6 *1090.2*
[m,m,m] 6 + 0	[m,m,m] 6 + 0	9	2.57–2.59 [m]	2.62–2.63	2.08	982.7 *1006.8*	[m,m,m] 6 + 0	9	2.46–2.52 [m]	2.40	1.99	1073.3 *1103.3*
[b,b,b] 6 + 0	[b,m,m] 6 + 0	10	2.65–2.75 [b] 2.59 [m]	2.62–2.76	1.99	983.5 *1007.5*	[m,m,m] 6 + 0	9	2.43–2.47 [m]	2.39–2.44	1.95	1075.1 *1104.0*
[b,b,b] 5 + 1[e]	[b,b,b] 5 + 1	11	2.62–2.73 [b]	2.65–2.78 4.56[c]	1.94	982.4 *1005.1*	[b,b,m] 5 + 1	10	2.41–2.56 [b] 2.38 [m]	2.42–2.62 4.28[c]	1.84	1073.9 *1103.0*
[b,b,b] 4 + 2	[b,b,b] 4 + 2	10	2.62–2.73 [b]	2.60–2.69 4.41–4.17[c]	2.01	983.4 *1009.0*						
[b,b,m] 5 + 1	[b,b,m] 5 + 1	10	2.62–2.73 [b] 2.54 [m]	2.62–2.70 4.29[c]	2.01	983.8 *1007.0*						
[b,b,m] 6 + 0	[b,b,m] 6 + 0	11	2.67–2.87 [b] 2.58 [m]	2.65–2.75	1.95	982.2 *1004.6*						

[a] Mono-*vs.* bidentate nitrate and m = w1 + w2 (first shell + second shell water molecules). [b] From HF/6-31G*//HF/6-31G* (first line) and DFT/6-31+G*//HF/6-31G* (*second line*) calculations in kcal mol^{-1}. [c] Second shell water molecule. [d] X-Ray structure of the $Eu(NO_3)_3(H_2O)_5$ complex.[25] [e] X-Ray structure of the $La(NO_3)_3(H_2O)_6$ complex.[26]


Initial structure *Final structure La(III)* *Final structure Lu(III)*

[b,b,b] *[b,b,b]* *[b,b,b]*

Fig. 3 Initial and optimized structures of model-built $Ln(NO_3)_3(H_2O)_4$ complexes (Ln = La, Lu).

in $Ln(NO_3)_3$. In the case of the Lu^{III} complex, two H_2O molecules migrated to the external sphere at 4.2 Å from the cation, forming strong hydrogen bonds to the two first shell H_2O molecules ($H_2O\cdots HOH$ distances are 1.80 and 1.83 Å), leading to a CN of 8.

Another minimization was performed on the Lu^{III} [b,b,b] complex, starting with somewhat longer Lu–O_{water} distances. It became [b,b,m] while the four water molecules remained coordinated to the metal, leading to a CN of 9. This 4 + 0 structure is, however, 4 kcal mol^{-1} less stable than the [b,b,b] 2 + 2 complex with 2 waters in the second shell.

The $Ln(NO_3)_3(H_2O)_5$ complexes. Five water molecules were added to the [m,m,m] and [b,b,b] $Ln(NO_3)_3$ complexes in such a way that O_{water} oxygens form a trigonal bipyramid, centred on the cation, with two axial O_{water} and three equatorial O_{water} oxygens placed along the N–Ln–N bisectors (5 + 0 water coordination; see Fig. 4). In the optimized structures (Fig. 4), the anion coordination mode depends somewhat on its initial state, but mono- and bidentate types co-exist for a given complex, due to changes in binding mode upon optimization. In the La^{III} complexes, the 5 H_2O molecules remained in the first shell. Thus, the cation coordination number, initially of 8 (for [m,m,m] nitrates) or 11 (for [b,b,b] nitrates), changed respectively to 9 (nitrates became [b,m,m]) or 10 ([b,b,m]). The final states of these two La^{III} complexes differ by 2 kcal mol^{-1}, indicating no marked preference.

In the Lu^{III} complexes, steric repulsions in the first shell are larger than in the La^{III} complexes, and three different structures were obtained. The initial [m,m,m] form became [b,m,m] and all five H_2O molecules remained in the first shell, leading to a CN of 10. Two optimizations of the [b,b,b] Lu^{III} complexes were performed, one starting with Lu–O_{water} distances of 2.45 Å as indicated above, and another one with somewhat shorter distances (about 2.3 Å). In both cases, one H_2O molecule migrated from the first to the second shell (4 + 1 water), while the four others remained at 2.3 to 2.5 Å in the first shell. The nitrates behave differently, though. In one case, they remained [b,b,b], leading to a CN of 10, while in the other case, one nitrate became monodentate to form a [b,b,m] complex with a CN of 9. The resulting [b,b,b] and [b,b,m] structures have similar energies ($\Delta E = 2$ kcal mol^{-1}), while the [b,m,m] form is less stable by about 6 kcal mol^{-1}.

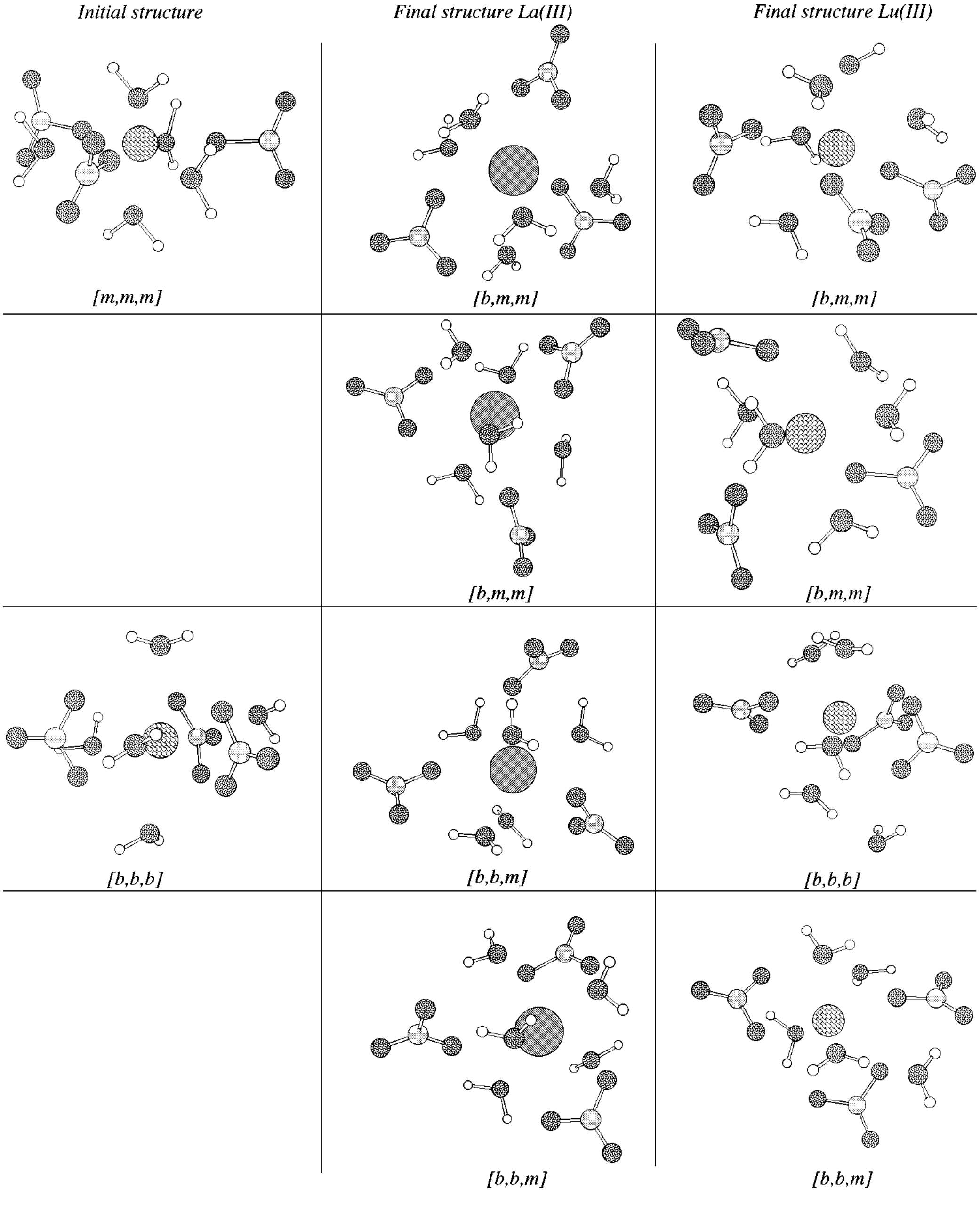


Fig. 4 Initial and optimized structures of model-built $Ln(NO_3)_3(H_2O)_5$ complexes (Ln = La, Lu).

For these La^{III} and Lu^{III} pentahydrate complexes, we also considered the X-ray structure of the $Eu(NO_3)_3(H_2O)_5$ analogue, which is of [b,b,b] type, but with a less symmetrical arrangement of the nitrates, compared to the model-built systems. The water "coordination" is of 4 + 1 type. After energy minimization, both lanthanum and lutetium complexes retain this mode of coordination, leading to a CN of 10. However, the corresponding energies are identical (for La^{III}) or somewhat less stable (by 3 kcal mol^{-1} for Lu^{III}) than for the model-built systems, indicating that the latter are reasonable.

The $Ln(NO_3)_3(H_2O)_6$ complexes. In the first series of model-built structures, six water molecules initially formed a network of D_{3h} symmetry (Fig. 5), with three H_2O above and three H_2O below the plane of the nitrogen atoms and the three nitrates were either monodentate [m,m,m] or bidentate [b,b,b]. This arrangement is reminiscent of the solid state structure of Lu^{III}$(H_2O)_9$.[27,28] After optimization, a dominant population of monodentate nitrates to both cations is observed (Fig. 5). In all cases, the six water oxygens sit in the first coordination shell (at 2.6 to 2.8 Å from La^{III} and 2.4 to 2.5 Å from Lu^{III}). This water coordination is detrimental to the nitrate coordination, which for La^{III} remains [m,m,m] in this starting form (leading to a CN of 9) and evolves from [b,b,b] to [b,m,m] in the other form (leading to a CN of 10). The two forms of this La^{III} hydrated complex have identical energies. For Lu^{III}, the initial [b,b,b] and [m,m,m] structures converge after optimization to a unique [m,m,m] type where the three anions are monodentate and the CN is 9. The energies of the [m,m,m] and [b,m,m] forms are also very close ($\Delta E = 2$ kcal mol^{-1}).

The above structures were compared with those derived from the X-ray structure of the $La(NO_3)_3(H_2O)_6$ complex, which is of [b,b,b] and 5 + 1 type with five water molecules coordinated to La^{III} (CN = 11).[26] After optimization with La^{III}, the nitrate and water coordination patterns remain similar, and the energy is within 1 kcal mol^{-1} identical to that of the model-built complexes. With Lu^{III}, one nitrate becomes monodentate ([b,b,m] type complex), leading to a CN of 10, but its energy is the same as for the model-built complexes.

For $La(NO_3)_3(H_2O)_6$, we further considered three alternative structures starting from the optimized model-built ones, but with different nitrate binding modes and/or different first plus second shell water molecules. One was of [b,b,b] type, but with 4 + 2 water molecules (CN = 10), obtained by adding 2 second shell H_2O molecules to the [b,b,b] 4 + 0 tetrahydrate. The two others were [b,b,m] with either 5 + 1 water (CN = 10) or 6 + 0 water (CN = 11), obtained respectively by adding one second shell H_2O molecule to the [b,b,m] 5 + 0 pentahydrate or by changing one nitrate from monodentate to bidentate in the [b,m,m] 6 + 0 hexahydrate. Based on the analysis of vibrational frequencies, the optimized structures were checked to correspond to energy minima. They all retained similar coordination features, leading to identical energies (within 1 kcal mol^{-1}) to the other models built from X-ray-derived starting structures, thus demonstrating the versatile structures of these complexes.

Concerning the Mulliken charge on the metal, it is close to 2.0 in all nitrate hydrates (from 1.95 to 2.09 for lanthanum and from 1.84 to 2.01 for lutetium complexes). The near constancy of this charge also reflects somewhat the similar energies of the several arrangements of the hydrates.

Nitrate coordination to lanthanide cations in the solid state

We analyzed the solid state structures of lanthanide nitrate hydrates $Ln(NO_3)_3(H_2O)_m$ reported in ref. 11 (see Table 3) and of lanthanide nitrate complexes retrieved from the Cambridge Crystallographic Structural Database (CCSD)[29] with La^{III},

Table 3 Characteristics of the solid state structures of $Ln(NO_3)_3(H_2O)_m$ hydrates[a]

Ln	w1 + w2	CN	Ln–O$_{nitrate}$/Å	Ln–O$_{water}$/Å	Ref.
La	5 + 1	11	2.62–2.88	2.53–2.67	26
Ce	5 + 1	11	2.59–2.88	2.49–2.64	30
Nd	4 + 2	10	2.55–2.72	2.43–2.46	31
Sm	4 + 2	10	2.52–2.72	2.41–2.43	32
Eu	4 + 1	10	2.47–2.63	2.40–2.50	25
Eu	4 + 1	10	2.47–2.58	2.42–2.50	11
Yb	4 + 1	10	2.38–2.57	2.30–2.39	33
Lu	3 + 0	9	2.37–2.44	2.28–2.30	11

[a] All nitrates are bidentate, m = w1 + w2 (first shell + second shell water molecules).

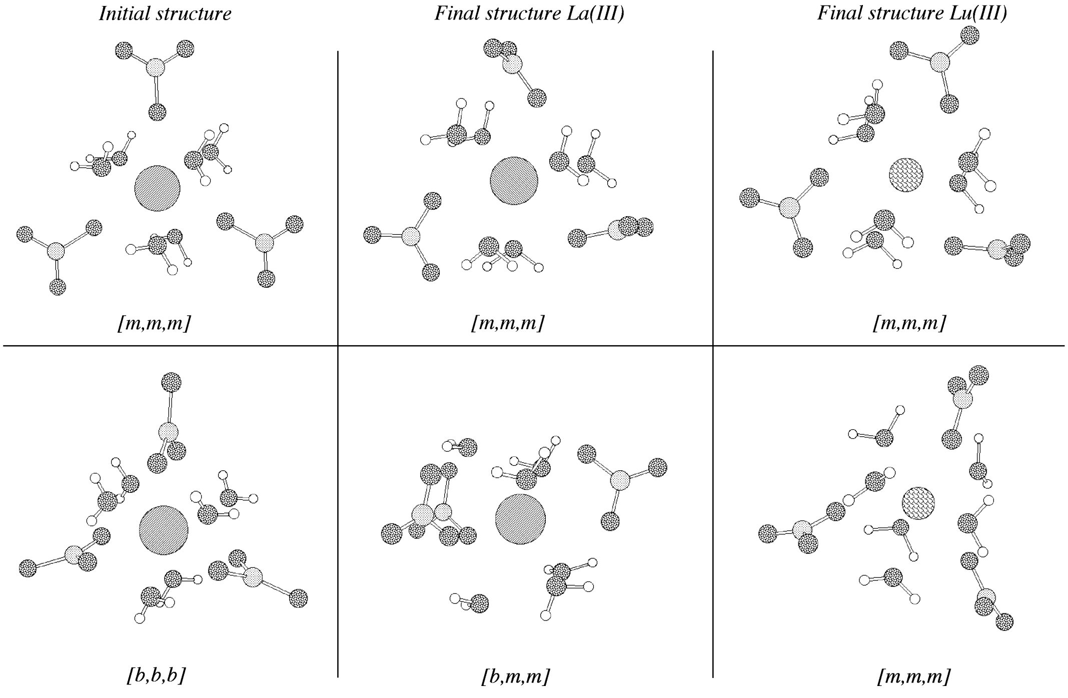


Fig. 5 Initial and optimized structures of model-built $Ln(NO_3)_3(H_2O)_6$ complexes (Ln = La, Lu).

Table 4 Statistical analysis of lanthanide coordination in the CCSD: number of structures, average metal coordination number (CN) (including all ligands; the number in parentheses corresponds to the number of structures in which all three nitrates sit in the first coordination sphere), metal–oxygen distances and their fluctuations

	N_{struct}	CN	Ln–O_{nitrate}/Å	Ln–O_{water}/Å
La	78(38)	10.4 ± 1.1	2.64 ± 0.06	2.57 ± 0.05
Eu	40(18)	9.7 ± 0.7	2.51 ± 0.07	2.42 ± 0.04
Lu	13(7)	9.2 ± 0.6	2.41 ± 0.06	2.30 ± 0.03

Eu^{III} and Lu^{III} as cations, skipping structures in which nitrates are complexed to two cations (Table 4). In the CCSD we found 78 complexes of La^{III}, 40 complexes of Eu^{III}, and 13 with Lu^{III}. Among them, 38, 18 and 7, respectively, contain the three nitrates in the first coordination sphere. The most important result is the lack of monodentate binding in trinitrato lanthanide complexes in the solid state. The resulting coordination number of the cation and the Ln–O_{nitrate} and Ln–O_{water} bonding distances are reported in Tables 3 and 4. They show that care should be taken when comparing the calculated *vs.* X-ray structures. In a crystal of a given $Ln(NO_3)_3(H_2O)_m$ complex, differences of up to 0.3 Å are observed for the different Ln–O_{nitrate} distances and of up to 0.1 Å for Ln–O_{water} distances. Generally, for a given metal, Ln–O_{nitrate} bonds are somewhat longer than the Ln–O_{water} ones, as expected from the larger effective size of the anionic oxygen atoms. The averages obtained from the CCSD fit the values found in the $Ln(NO_3)_3(H_2O)_m$ hydrates and follow the same trends as our calculated results: from La^{III} to Lu^{III}, the Ln–O distances decrease by about 0.2–0.3 Å and the coordination numbers decrease by about one unit.

In structures retrieved from the CCSD and containing three nitrates in the first shell, the latter are bidentate and the first coordination sphere is completed by other ligands. The average coordination number CN of the cation is 10.4 ± 1.1 for La^{III}, 9.7 ± 0.69 for Eu^{III} and 9.2 ± 0.55 for Lu^{III}. These values are about one unit larger than those with only water as ligands in the aqueous phase as well as in solid state structures, where CN ranges from 9 for La^{III} to 8 for Lu^{III}.[7,34–36] They are somewhat smaller than in the "maximally hydrated" complexes, where CNs are 11, 10 and 9, respectively (Table 3).[11]

Conclusions

We report here the QM optimized structures and binding energies (ΔE) of $Ln(NO_3)_n^{(3-n)+}$ complexes (n = 1–3), which show that in these unsaturated complexes bidentate binding is intrinsically preferred over monodentate binding by about 20–35 kcal mol^{-1}. The largest difference is found in the $Lu(NO_3)^{2+}$ complex, while the smallest is found for the $La(NO_3)_3$ complex, indicating that the preference for bidentate binding decreases when the number of anions increases (because the anion–anion repulsions are larger with bidentate than with monodentate anions) and the cation becomes less hard. DFT calculations yield the same conclusions, but the difference is somewhat smaller. This energy difference is small, compared to the interaction energy between one lanthanide cation and a single water molecule (about 90 kcal mol^{-1}), which suggests that water binding to the cation may shift the preference towards monodentate binding. This is supported by optimizations of neutral $Ln(NO_3)_3(H_2O)_m$ hydrates (m = 4–6) where nitrates are initially monodentate or bidentate, leading to cation coordination numbers ranging from 9 to 11 for La^{III} and from 8 to 10 for Lu^{III}. As the number of water molecules is increased, some evolution from bidentate to monodentate binding modes is observed, which become of similar energies at both HF and DFT levels of theory. One important problem in molecular modeling concerns the conformational sampling of the system, and all possible arrangements of the ligands cannot be considered. We, however, explored a number of typical coordinations ranging from all-monodentate to all-bidentate modes, as well as of water distributions between the first and second shell, including X-ray-derived structures where all nitrates are bidentate. The most important result is the lack of a clear-cut preference for bidentate nitrate binding for these hydrates in the gas phase. Instead, the two binding modes are nearly isoenergetic and correspond to different hydration numbers. Adding one water molecule to the tetrahydrated lanthanum complex is exothermic (by about 13 kcal mol^{-1} at the HF level and 14 kcal mol^{-1} at the DFT level), whether this molecule is added in the second shell (strong hydrogen bonds with the first shell water plus cation–dipole interactions) or in the first shell (larger cation–dipole interactions compensated for by intrashell repulsions). Moving from the pentahydrated (m = 5) to the "maximally hydrated"[11] lanthanum complexes (m = 6) is exothermic by a similar amount, leading to an equilibium between 6 + 0, 5 + 1 and 4 + 2 water distributions in the two shells. Generally the largest (/smallest) water coordination (6 + 0) corresponds to monodentate (/bidentate) nitrates. These results support the MD simulation results, according to which in aqueous solution, nitrates move from bidentate to monodentate coordination on their pathway to dissociation. In solution, however, enthalpic and entropic energy components are antagonistic. Bidentate binding may be favoured by entropy, as this reduces the number of "frozen" water molecules coordinated to the cation. According to one referee, this entropy effect amounts to about 13 kcal mol^{-1}, which is comparable to our calculated energy stabilization brought about by coordination of one extra water molecule to saturated complexes. On the other hand, monodentate binding may be favoured from an enthalpic point of view, related to second shell hydration, as up to six hydrogen bonds can form with the "exo" O_{NO_3} oxygens of three monodentate nitrates, instead of three hydrogen bonds with bidentate nitrates.[32] Thus, in solution, hydrated nitrate complexes may display an equilibrium between several forms of polyhydrated species involving different types of nitrate binding modes. The contrast with the binding patterns observed in solid state structures, where nitrates are generally bidentate, suggests that the latter are likely stabilized by additional forces, like crystal packing and/or dielectric effects.[37] What happens in concentrated aqueous solution can in principle be investigated by X-ray scattering methods,[38,39] but the latter may not be precise enough to reach a firm conclusion on the nitrate binding mode. Increasing the nitrate salt concentration may also perturb the environment of the complex, making comparisons with gas phase data still more problematic.

Acknowledgements

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37 From a computational point of view, accounting for such second hydrogen bonding interactions would require an explicit representation of all second shell molecules. An empirical solvation model based, for instance, on polarizable cavity models, may not be appropriate for that purpose. Using the SCI-PCM model, we calculated the "solvation energy" of the hexahydated $La(NO_3)_3 \cdot 6H_2O$ complexes with the $6+0$, $5+1$ and $4+2$ water arrangements, and found their "solvation" energy to differ by less than 1 kcal mol^{-1}.

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