78. Lanthanide-Nitrate Interaction in Anhydrous Acetonitrile and Coordination Numbers of the Lanthanide Ions: FT-IR Study[1])

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The interaction between lanthanide ions Ln^{III} (Ln = La, Nd, Sm–Dy, Er, Yb) and nitrate ions is investigated by FT-IR spectroscopy in dilute anhydrous MeCN solution. The work is performed for ratios $R = [NO_3^-]_t/[Ln^{III}]_t$ ranging from 0 to 8 and for solutions generally 0.05M in Ln^{III}, prepared from anhydrous lanthanide perchlorates $Ln(ClO_4)_3$. When nitrate is progressively added to the $Ln(ClO_4)_3$ solutions, the formation of $[Ln(NO_3)_n]^{(3-n)+}$ species is clearly evidenced by the FT-IR spectra. All the NO_3^- ions are coordinated and bidentate. A quantitative study was performed using the ν_1 and ν_6 vibrational modes for coordinated NO_3^- ions. The average coordination numbers estimated for Nd, Eu, Tb, and Er in solutions of trinitrates are 9.0, 9.1, 8.3, and 8.2, respectively (±0.3 unit). In presence of an excess NO_3^-, these numbers become 9.8, 10.2, 10.0, 9.8, 9.9, and 9.9 (±0.3 unit) for La, Nd, Eu, Tb, Er, and Yb, respectively. No hexanitrato species forms under the experimental conditions used (R up to 8). The structural aspect of the various nitrato species is also investigated. In the pentanitrato species, all the ligands appear to be equivalent, while large inequivalences are observed for $Ln(NO_3)_3$ solutions. Since for the latter most of the absorption bands assigned to nitrate vibrations contain several components, a curve-fitting procedure has been used for decomposing the ν_2, ν_4, and ν_6 vibrations. There is a considerable difference between Ln^{III} ions, the nitrate inequivalences being larger in the middle of the series.

Introduction. – During the last decades, there has been a growing interest in the use of lanthanide ions as probes in biochemical systems [1]. This has prompted numerous studies about the coordination properties of these ions, particularly in solution. In the case of trivalent lanthanide ions, this information is difficult to acquire in view of their high kinetic lability, their nondirectional chemical bonding, and the range of large coordination numbers they can display. A recent paper reviews the subject in aqueous solutions [2]. The coordination numbers of Ln^{III} ions and their interaction with anions and neutral molecules in organic solvents have been systematically investigated in our laboratory by means of UV/VIS absorption spectroscopy [3], luminescence [4–8], ^{139}La-NMR [9], and *Fourier*-transform infrared spectroscopy (FT-IR) [6] [7] [10–14].

Studies of the lanthanide-nitrate interaction as well as the determination of stability constants and thermodynamic parameters have been performed in various solvents, *e.g.* aqueous and anhydrous alcohols [15], dimethylformamide [3] [4] [7] [16] [17], dimethylacetamide [18], dimethylsulfoxide [19], and H_2O/acetone mixtures [20]. In anhydrous MeCN, conductimetric measurements on dilute solutions of Nd, Eu, or Tb nitrates indicate that no dissociation occurs [3] [6] [10]. Moreover, the nitrato group frequencies are consistent with bidentate anions having C_{2v} local symmetry.

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[1]) Part 13 of the series 'FT-IR and Fluorometric Investigation of Rare-Earth and Metal Ion Solvation'; Part 12: [14].

In this communication, we present a detailed FT-IR study of the lanthanide-nitrate interaction in anhydrous MeCN for selected light (La, Nd), intermediate (Sm, Eu, Gd, Tb, Dy), and heavy (Er, Yb) lanthanide cations. The coordination number of the Ln^{III} ions, in presence of an excess nitrate, is determined, and the structural aspects of the various nitrato species are discussed.

Experimental. – Hydrated lanthanide nitrates and perchlorates were prepared from pure oxides (99.99%, *Research Chemicals* or *Glucydur*) and reagent-grade HNO_3 or $HClO_4$ (*Merck*). Complete dehydratation of the salts was performed by stepwise heating under high vacuum (10^{-6} mm Hg) during 3–6 weeks. The absence of H_2O in anhydrous salts was confirmed by IR spectroscopy and *Karl Fischer* titration (*Mettler DL 18*). Anal.-grade $AgNO_3$ (*Merck*) was used after drying *in vacuo* (10^{-2} mm Hg) at 60–100°. The $[Yb(Bu_4N)(NO_3)_5]$ complex was synthesized according to [21]. MeCN (*Fluka*) was dried as described in [14]; its H_2O content measured by *Karl Fischer* titration was 30 ppm. All the solns. were prepared in a dry glove-box under N_2 containing less than 10 ppm H_2O. Lanthanide-ion concentrations, usually 0.05M, were determined by complexometric analysis (*Titriplex III, Merck*, in presence of urotropine and xylene-orange).

FT-IR Difference spectra were recorded with an *IFS-113v Bruker* vacuum spectrometer, under the following conditions: 1-cm^{-1} bandpass, 600 scans, 4-point (trapezoidal) apodization, optical path 50 or 23 μm. The cell thickness was determined before each measurement, according to the interference fringe procedure [14]. Liquid cells for IR measurements were filled in the dry glove-box. Curve analysis of the IR spectra into their individual components was performed on a *VAX-8850* computer using *Lorentz*ian functions to simulate the absorption lines [22]. The quantitative results given below are averages of several measurements performed on independently prepared solns. *Raman* spectra were recorded on a *Ramalog-4* spectrometer from *Spex Industries*.

Results and Discussion. – *$Ln(NO_3)_3$ in Anhydrous MeCN.* The isolated NO_3^- ion belongs to the D_{3h} point group; it has four normal vibrational modes, $\nu_1(A_1')$, $\nu_2(A_2'')$, $\nu_3(E')$, and $\nu_4(E')$, observed at *ca.* 1050 cm^{-1} (*Raman* only), 830 cm^{-1} (IR only), 1390 cm^{-1} (IR, R) and 720 (IR, R) cm^{-1}, respectively [23]. The anion can bind a metal ion in four different ways: monodentate, bidentate, and bridging (either bidentate or tridentate). In solution, only the second coordination mode has been observed and the local symmetry is lowered to C_{2v} (or C_s). This leads to a splitting of the ν_3 and ν_4 bands into $\nu_1(A_1)$, $\nu_4(B_2)$, and $\nu_3(A_1)$, $\nu_5(B_2)$, respectively; $\nu_1(A_1')$ becomes $\nu_2(A_1)$ and IR-allowed, while $\nu_2(A_2'')$ becomes $\nu_6(B_1)$. The strength of the metal-nitrate interaction is best characterized by the splitting of the $\nu_3(E')$ mode: $\tilde{\nu}_1(A_1) - \tilde{\nu}_4(B_2)$.

Lanthanide nitrates behave as non electrolytes in anhydrous MeCN. The molar conductivities of 0.01M solutions are: 13 (Nd), 15 (Eu), 10 (Tb), and 7 (Er) $\Omega^{-1} \cdot cm^2 \cdot M^{-1}$. The observed nitrato group frequencies, *Raman* polarizations [8], and $\tilde{\nu}_1 - \tilde{\nu}_4$ splittings are consistent with bidentate nitrate ions having approximate C_{2v} local symmetry (*Table 1*).

Most of the absorption bands assigned to nitrate vibrations contain at least two components, as has been observed for solid samples of anhydrous trinitrates [24]. This may be explained either by an interaction between vibrations of the nitrato groups bonded to the same cation, or by the presence of inequivalent NO_3^- ions, *e.g.* coordinated at slightly different distances. In view of the large differences observed between the various Ln's (*vide infra*), we interpret our data taking the latter explanation into account. To better characterize these components, we have applied a curve-fitting procedure to the ν_2, ν_4, and ν_6 vibrational modes (*Fig. 1, Tables 2* and *3*). Since ν_1 interferes with a solvent band, a trustful decomposition could not be performed on this vibration. The relative band areas give an idea of the relative concentration of each nitrato species. However, it

Table 1. *Nitrate Vibrations* [cm^{-1}] *in* $Ln(NO_3)_3$ *Solutions 0.05* M *in Anhydrous MeCN*[a][b])

	La[c])	Nd	Sm	Eu	Tb	Dy	Er	Yb
ν_1(ext.)	1510 (sh)	1511 (sh)	1540 (sh)	1540 (sh)	1540 (sh)	1537 (sh)	1540 (sh)	1536 (sh)
			1516 (*s*)	1510 (*s*)	1510 (*s*)	1518 (*s*)	1514 (*s*)	1520 (*s*)
ν_1(int.)	1490 (*s*)	1489 (*s*)	1498 (*s*)	1489 (*s*)	1489 (*s*)	1498 (*s*)	–	1504 (sh)
ν_4(int.)	1299 (*s*)	1303 (*s*)	1305 (*s*)	1303 (*s*)	1303 (*s*)	1316 (sh)	1296 (sh)	1301 (sh)
						1292 (*s*)		
ν_4(ext.)	–	1284 (sh)	1282 (*s*)	1284 (*s*)	1284 (*s*)	1282 (*s*)	1284 (*s*)	1289 (*s*)
ν_2	1029 (*m*)	1030 (*m*)	1031 (*m*)	1030 (*m*)	1030 (sh)	1031 (sh)	1026 (*m*)	1029 (*m*)
		1023 (sh)	1023 (sh)	1023 (sh)	1023 (*m*)	1025 (*m*)	–	–
ν_6	818 (*w*)	818 (*w*)	818 (*w*)	818 (*w*)	815 (*w*)	816 (*w*)	814 (*w*)	814 (*w*)
		816 (sh)	815 (sh)	814 (*w*)	–	–	–	–
ν_3	735 (*w*)	739 (*w*)	742 (*w*)	741 (*w*)	745 (*w*)	745 (*w*)	750 (*w*)	752 (*w*)
ν_1(ext.) – ν_4(ext.)	–	227	234	226	226	236	230	231
ν_1(int.) – ν_4(int.)	191	186	193	186	186	206	–	203

[a]) (*s*): strong; (*m*): medium; (*w*): weak; (sh): shoulder; ν(ext.) and ν(int.) represent the components of ν_1 and ν_4 yielding the largest and the smallest splitting, respectively. When several components are observed, the splitting is calculated between the strongest components. [b]) ν_5 is observed in the *Raman* spectra only, around 715 cm^{-1} [c]) $c = 0.016$M.

Table 2. *Curve Analysis* (2 and 3 components) *of the* ν_4 *Vibration of Bonded Nitrate in* $Ln(NO_3)_3$ *Solutions 0.05* M *in Anhydrous MeCN*[a])

Ln	ν_4^1 [cm^{-1}]	s_4^1 (±0.3)	ν_4^2 [cm^{-1}]	s_4^2 (±0.3)	$\Sigma\Delta^2$ (×10^3)	ν_4^1 [cm^{-1}]	s_4^1 (±0.3)	ν_4^2 [cm^{-1}]	s_4^2 (±0.3)	ν_4^3 [cm^{-1}]	s_4^3 (±0.3)	$\Sigma\Delta^2$ (×10^3)
La[b])	1298.0	2.0	1285.0	1.0	2.5	–	–	–	–	–	–	–
Nd	1302.5	2.1	1284.5	0.9	4.1	1303.6	1.9	1291.1	0.7	1279.1	0.4	2.9
Sm	1305.5	1.6	1282.3	1.4	5.2	1306.4	1.4	1287.1	1.2	1276.8	0.4	2.9
Eu	1302.6	1.1	1283.6	1.9	2.1	1309.4	1.1	1289.0	1.1	1278.7	0.8	1.0
Gd	1308.2	0.9	1283.6	2.1	6.7	1310.1	0.8	1289.6	1.2	1278.7	1.0	3.4
Tb	1304.8	0.6	1284.6	2.4	6.5	1310.9	0.4	1290.8	1.4	1279.9	1.2	3.4
Dy	1291.9	2.4	1282.1	0.6	6.7	1315.4	0.2	1293.0	1.7	1282.3	1.1	2.2
Er	1296.8	1.4	1284.9	1.6	3.6	1298.5	1.2	1290.6	1.1	1283.2	0.7	3.0
Yb	1301.2	1.6	1290.0	1.4	2.8	1301.8	1.6	1291.8	0.9	1285.5	0.5	1.7

[a]) s is the relative band area (total band area = 3.0); $\Sigma\Delta^2$ is the goodness-of-fit parameter. [b]) 0.016M.

Table 3. *Curve Analysis into Two* Lorentzian *Components of the* ν_2 *and* ν_6 *Vibrational Modes of Bonded Nitrates in* $Ln(NO_3)_3$ *Solutions 0.05* M *in Anhydrous MeCN*[a])

Ln	ν_i	ν_i^1 [cm^{-1}]	s_i^1 (±0.3)	ν_i^2 [cm^{-1}]	s_i^2 (±0.3)	$\Sigma\Delta^2$ (×10^3)	ν_i	ν_i^1 [cm^{-1}]	s_i^1 (±0.3)	ν_i^2 [cm^{-1}]	s_i^2 (±0.3)	$\Sigma\Delta^2$ (×10^3)
La[b])	ν_2	1029.0	3.0	–	–	0.7	ν_6	818.3	3.0	–	–	0.6
Nd		1030.1	2.6	1022.5	0.4	0.6		818.1	1.8	815.8	1.2	0.3
Sm		1030.9	1.6	1023.1	1.4	3.7		817.9	0.9	815.1	2.1	1.3
Eu		1031.1	1.4	1023.4	1.6	1.5		817.5	0.9	814.4	2.1	0.3
Gd		1031.2	0.8	1023.6	2.2	1.5		817.5	1.0	814.6	2.0	0.6
Tb		1032.1	0.7	1023.8	2.3	1.1		815.8	1.7	813.7	1.3	0.5
Dy		1031.5	0.5	1025.1	2.5	2.8		816.0	0.6	814.6	2.4	0.9
Er		1026.0	2.0	1024.3	1.0	0.7		815.8	1.7	813.2	1.3	0.4
Yb		1028.4	2.1	1025.7	0.9	1.1		815.6	0.9	813.5	2.1	0.9

[a]) s_i is the relative band area (total band area = 3.0); $\Sigma\Delta^2$ is the goodness-of-fit parameter. [b]) 0.016M.

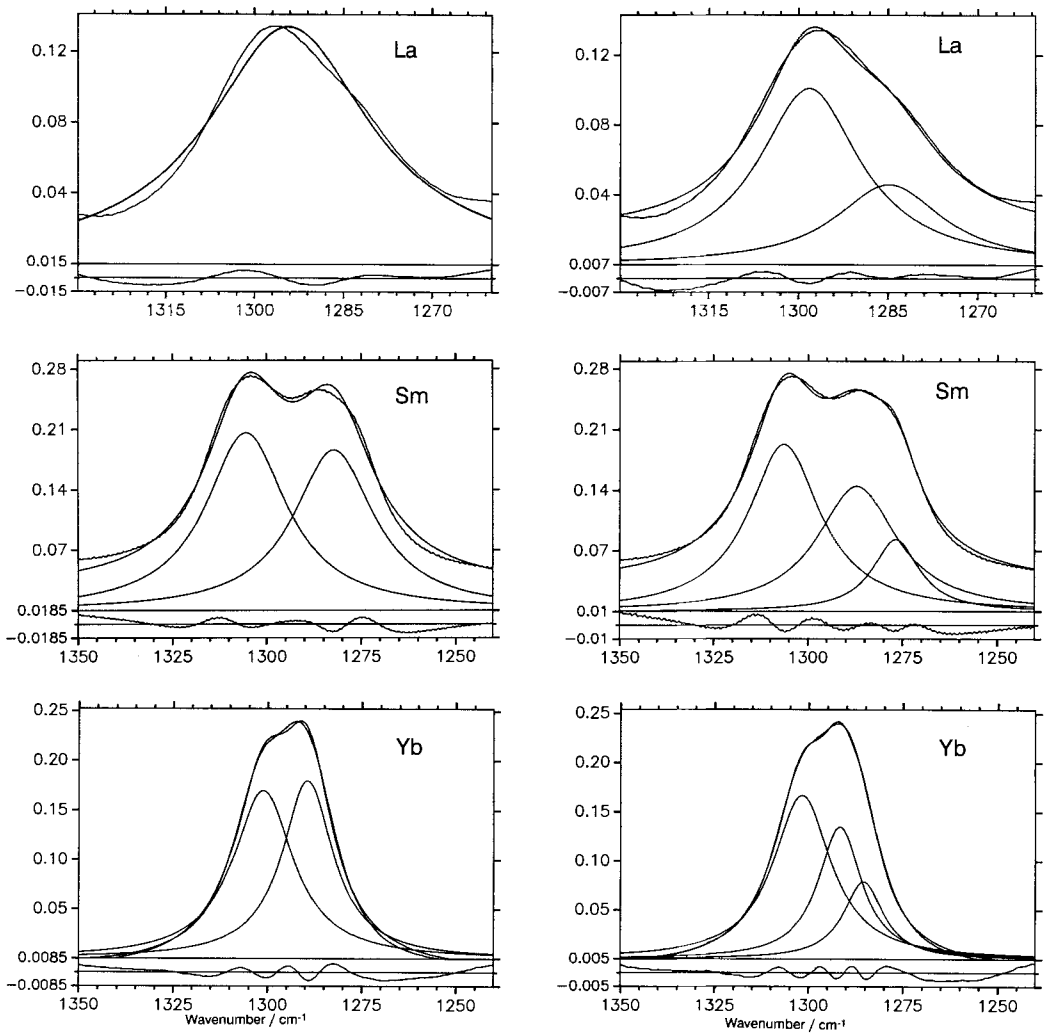

Fig. 1. *Curve analysis of the FT-IR difference spectra* (absorption units) *of* $Ln(NO_3)_3$ *solutions 0.05* M *in anhydrous MeCN*

cannot be directly translated into these concentrations, since the absorption coefficients vary with the polarization of the nitrate which, in turn, varies with the strength of the chemical bond.

For ν_4, the goodness-of-fit parameters $\Sigma\Delta^2$ are smaller, when the band profile is resolved into three components, especially for Dy and with the exception of La, which displays only two components. The shape of the band changes considerably along the series, and the general trends are as follows. *i*) The component at higher wavenumbers, around 1300 cm^{-1}, is the more intense for La, Nd, Sm, and for Er, Yb. *ii*) Inequivalences are largest for the ions in the middle of the series. In particular, Eu and Gd display three

components with approximately the same intensity. Moreover, the total splitting amounts to 13–16 cm^{-1} for La, Er, and Yb, while it ranges between 25 and 33 cm^{-1} for the other ions.

The ν_2 and ν_6 vibrations can be decomposed into two components only. The addition of a third constituent does not improve much the fit and the splitting between the last two components is very small (1–3 cm^{-1}). The symmetric stretching mode ν_2 gives rise to a unique band for La. A second component appears at *ca.* 8 cm^{-1} lower for Nd, and its intensity increases sharply to reach 50% (Sm, Eu), 75% (Gd, Tb), and 83% (Dy) of the total band area. The situation for Er and Yb is alike that observed for La, with two closely spaced components (2–3 cm^{-1}) having a relative band area of 2:1. The ν_6 mode displays only a small splitting. Again, there is only one component for La, while two closely spaced components (2–3 cm^{-1}) are observed for the other Ln's. Due to this small separation, large uncertainties are associated with the relative band areas, preventing a detailed analysis, but the general trend is similar to the one evidenced for ν_2.

Since ν_1 could not be mathematically decomposed, we determined the $\tilde{\nu}_1 - \tilde{\nu}_4$ splittings from the experimental data and have, therefore, defined two splittings for each ion (*Table 1*). These are based on the two main components of ν_1 and ν_4 defined with respect to the vibration ν_3 of the free ion: the *internal* ones corresponding to nitrates interacting more weakly (*i.e.* with longer Ln–NO_3^- distances) and the *external* ones, related to nitrates interacting more strongly (*i.e.* with shorter Ln–NO_3^- distances). The average $\tilde{\nu}_1$(ext.) – $\tilde{\nu}_4$(ext.) and $\tilde{\nu}_1$(int.) – $\tilde{\nu}_4$(int.) splittings amount to 230±4 and 193±13 cm^{-1}, respectively, and are both well within the range accepted for bidentate coordination [23]. They point to a rather strong Ln-nitrate interaction. Assuming that the $\tilde{\nu}_1 - \tilde{\nu}_4$ splittings represent a measure of the Ln–nitrate distance [25], a schematic representation of the different trinitrato species can be established (*Fig. 2*). *Kavun et al.* [25] have also observed a splitting of the ν_1 and ν_4 vibrations ($\Delta\tilde{\nu} \approx 10$ cm^{-1}) for $Ln(NO_3)_3$ solutions in acetone containing H_2O (Ln = Tm, Yb; H_2O/Ln = 3–18) and have concluded to the existence of differently coordinated NO_3^- groups. In these solutions, the average $\tilde{\nu}_1 - \tilde{\nu}_4$ splitting amounts to 200 cm^{-1}, indicating that the Ln-nitrate interaction is slightly weaker than in anhydrous MeCN.

In addition to nitrate vibrations, the spectra display bands from coordinated MeCN molecules. Four vibrational modes of are substantially blue-shifted upon complexation [6]: ν_8(CCN), ν_4(C–C), ν_2(C≡N), and the combination ν_3(HCN) + ν_4(C–C) at *ca.* 395–405 (+20 to +25), 935–940 (+20), 2275–2285 (+23 to +33) and 2305–2315 (+14 to +21) cm^{-1}, respectively.

Formation of Pentakis(nitrato) Species in Anhydrous MeCN. When increasing amounts of $AgNO_3$ are added to anhydrous solutions of lanthanide perchlorates, the quantitative formation of successive $[Ln(NO_3)_n]^{(3-n)+}$ species (n = 1–5) is clearly evidenced by the FT-IR spectra (*Fig. 3*), the vibrational modes of uncoordinated nitrate being absent from the spectra up to $R = [NO_3^-]_t/[Ln^{III}]_t = 5$. As was demonstrated by *Bünzli* and *Kasparek* [12], the ClO_4^- ion forms inner-sphere complexes with lanthanides in anhydrous MeCN. Indeed, $Ln(ClO_4)_3$ solutions ($R = 0$) display small absorption bands, besides the two IR-active modes of uncoordinated perchlorate (u, T_d symmetry), which we assign to monodentate (m, C_{3v}) and bidentate (b, C_{2v}) perchlorate moieties. When an increasing amount of nitrate is added to the perchlorate solutions, the Ln-perchlorate interaction decreases progressively. For $R > 2$, the vibrational mode of bidentate

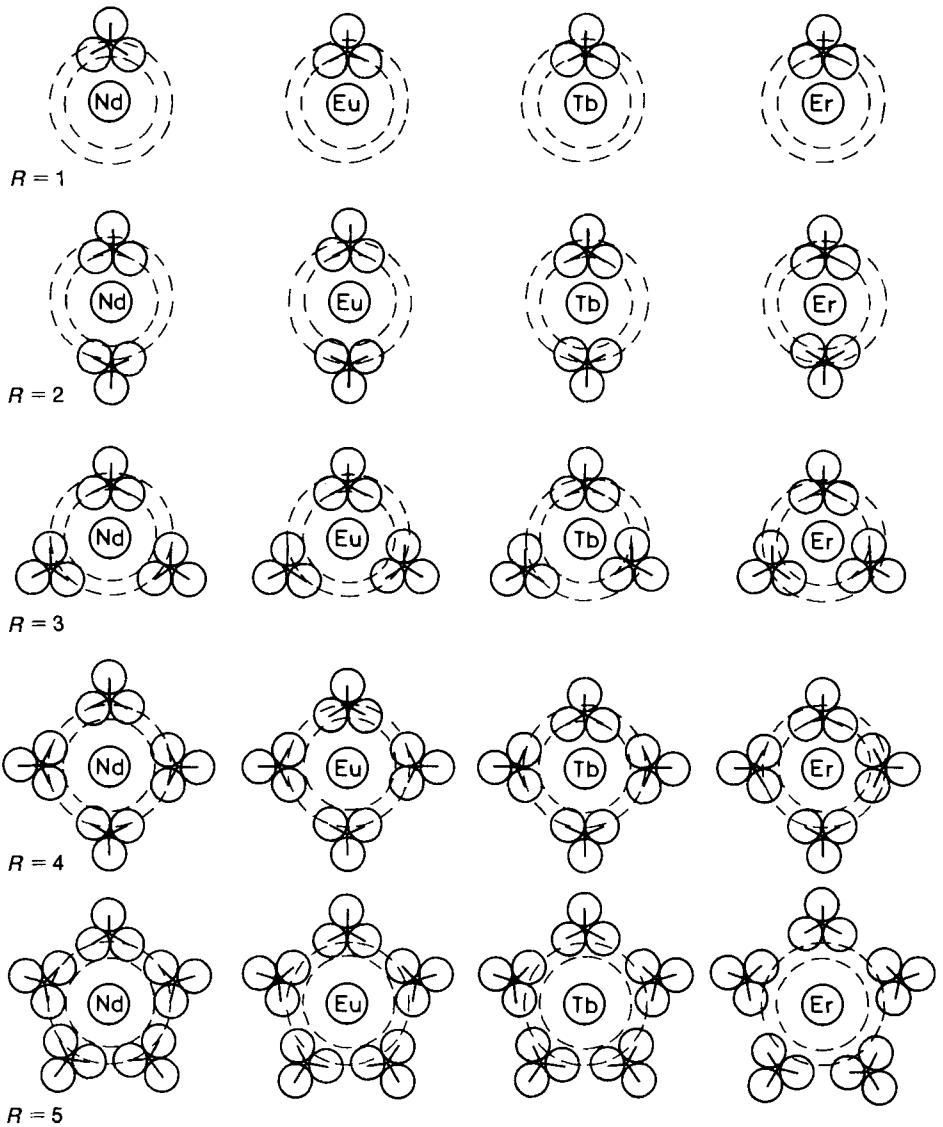

Fig. 2. *Schematic representation of various nitrato species in anhydrous MeCN* (see text for an explanation). $R = [NO_3^-]_t/[Ln]_t$.

perchlorates are generally no more observed. Monodentate perchlorates are present up to $R = 4$, while all the ClO_4^- is uncoordinated for larger values of R. A quantitative study of the ionic perchlorate was performed using the $\nu_3(i)$ vibration ($\varepsilon = 2270 \pm 35$ M^{-1} cm^{-1} [12]). The average number of ionic ClO_4^-, $\bar{n}_u$, increases with R, reaching a maximum around $R = 3$, while the absorbance A_{max} ($\nu_3 + \nu_4$) of bonded MeCN molecules decreases to reach zero for $R = 5$. Simultaneously, the $\nu_3 + \nu_4$ component related to Ag-bonded solvent molecules becomes more important. The replacement of both ClO_4^- and MeCN by nitrate

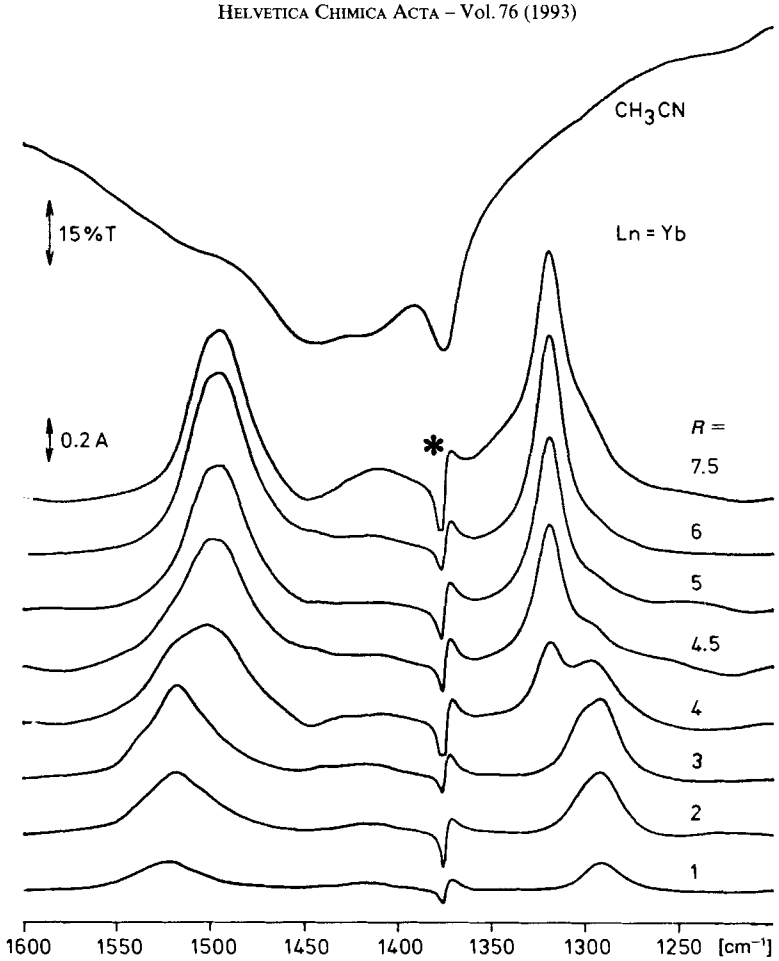

Fig. 3. *Part of the FT-IR difference spectra of $Yb(ClO_4)_3$ solutions in anhydrous MeCN, in presence of various amounts of nitrate.* $R = [NO_3^-]_t/[Ln]_t$. The upper trace represents the transmission spectrum of MeCN. The star denotes an incomplete compensation of the solvent.

in the first coordination sphere (*Fig. 4*) is confirmed by the study of the Ln–O(NO_3^-) vibrations (Ln = Nd, Eu, Tb, Er) which occur in the range of 220–240 cm^{-1} (in the solid state, this mode is observed between 240 and 270 cm^{-1} [26]). For $R = 1$, the Ln–O(NO_3^-) mode is observed at *ca.* 230 cm^{-1}, while for $R = 5$ its energy decreases to *ca.* 220 cm^{-1}. The Eu–O(ClO_4^-) mode appears at 217 cm^{-1} [5].

The nitrate vibrations ν_2, ν_4, and ν_6 undergo a hypsochromic shift as R increases while ν_1 and ν_3 experience a bathochromic shift (*Table 4*). Depending upon the Ln ion and the ratio R, some of the vibrational modes are split into 2–3 components. When $R > 5$, absorption bands of uncoordinated nitrate ($\tilde{\nu}_3 = 1340\ cm^{-1}$, $\tilde{\nu}_2 = 833\ cm^{-1}$) as well as those of the bidentate nitrate bonded to the Ag^+ ion ($\tilde{\nu}_1 = 1412\ cm^{-1}$, $\tilde{\nu}_4 = 1302\ cm^{-1}$, $\tilde{\nu}_2 = 1036\ cm^{-1}$, $\tilde{\nu}_6 = 825\ cm^{-1}$) appear in the spectra. We have checked that the observed FT-IR spectra for $R = 3$ and 5 are identical to those of solutions containing pure $Ln(NO_3)_3$ or

Table 4. *Observed Vibrations* [cm^{-1}] *of Coordinated Nitrate in* $Ln(ClO_4)_3$ *Solutions 0.05* M *in Anhydrous MeCN Containing Nitrate*[a])

Vibration	R	La	R	Nd	R	Eu	R	Tb	R	Er	R	Yb
ν_1	1.5	1498 (*s*)	1.0	1520 (*s*)	1.1	1523 (*s*)	1.3	1522 (*s*)	1.0	1520 (*s*)	1.0	1523 (*s*)
		–		1490 (sh)		1500 (sh)		1500 (sh)		1500 (sh)		–
	3.0	1520 (sh)	3.0	1520 (sh)	3.1	1520 (sh)	2.8	1530 (sh)	3.0	1530 (sh)	3.0	1534 (sh)
		1490 (*s*)		1490 (*s*)		1496 (*s*)		1522 (*s*)		1520 (*s*)		1518 (*s*)
		–		1475 (sh)		–		1500 (sh)		1500 (sh)		–
	5.0	1464 (*s*)	5.0	1490 (*s*)	5.0	1491 (*s*)	5.0	1492 (*s*)	5.0	1493 (*s*)	5.0	1495 (*s*)
		–		1475 (sh)		–		–		–		–
ν_4	1.5	1289 (*s*)	1.0	1295 (sh)	1.1	1282 (*s*)	1.3	1283 (*s*)	1.0	1287 (*s*)	1.0	1291 (*s*)
		–		1278 (*s*)		–		–		–		–
	3.0	1300 (*s*)	3.0	1303 (*s*)	3.1	1309 (*s*)	2.8	1310 (sh)	3.0	1310 (sh)	3.0	1302 (sh)
		–		1285 (sh)		1287 (*s*)		1285 (*s*)		1293 (sh)		1294 (*s*)
		–		–		–		–		1286 (*s*)		–
	5.0	1324 (*s*)	5.0	1325 (sh)	5.0	1310 (*s*)	5.0	1311 (*s*)	5.0	1316 (*s*)	5.0	1319 (*s*)
		–		1305 (*s*)		–		–		–		–
ν_2[b])	1.5	1029 (sh)	1.0	1025 (sh)	1.1	1025 (sh)	1.3	1025 (sh)	1.0	1027 (sh)	1.0	1029 (sh)
	3.0	1035 (sh)	3.0	1029 (*m*)	3.1	1032 (*m*)	2.8	1031 (sh)	3.0	1035 (sh)	3.0	1029 (*m*)
		1029 (*m*)		–		1028 (sh)		1025 (*m*)		1025 (*m*)		–
	5.0	1028	5.0	1028 (*m*)	5.0	1030 (*m*)	5.0	1030 (*m*)	5.0	1030 (*m*)	5.0	1032 (*m*)
ν_6	1.5	817 (*w*)	1.0	814 (*w*)	1.1	813 (*w*)	1.3	813 (*w*)	1.0	813 (*w*)	1.0	814 (*w*)
	3.0	819 (*w*)	3.0	818 (*w*)	3.1	818 (*w*)	2.8	815 (*w*)	3.0	815 (*w*)	3.0	815 (*w*)
		–		–		816 (*w*)		817 (sh)		–		–
	5.0	822 (*w*)	5.0	819 (*w*)	5.0	818 (*w*)	5.0	817 (*w*)	5.0	817 (*w*)	5.0	817 (*w*)
ν_3	1.5	741 (sh)	1.0	745 (*w*)	1.1	748 (*w*)	1.3	755 (*w*)	1.0	755 (*w*)	1.0	757 (*w*)
		738 (*w*)		742 (sh)		–		–		–		–
	3.0	734 (*w*)	3.0	740 (*w*)	3.1	748 (*w*)	2.8	755 (sh)	3.0	754 (*w*)	3.0	752 (*w*)
		–		–		743 (sh)		745 (*w*)		–		–
	5.0	734 (*w*)	5.0	737 (*w*)	5.0	740 (*w*)	5.0	743 (*w*)	5.0	745 (*w*)	5.0	749 (*w*)
$\nu_1 - \nu_4$[c])	1.5	209	1.0	242	1.1	241	1.3	239	1.0	233	1.0	232
	3.0	190	3.0	187	3.1	187–209	2.8	237	3.0	234	3.0	224
	5.0	140	5.0	185	5.0	181	5.0	181	5.0	177	5.0	176

[a]) $R = [NO_3^-]_t/[Ln]_t$; (*s*): strong; (*m*): medium; (*w*): weak; (sh): shoulder.

[b]) ν_2 is partially masked by the ν_1 vibration of monodentate perchlorate.

[c]) When several components are observed, the average $\nu_1 - \nu_4$ splitting is calculated as difference between the strongest components.

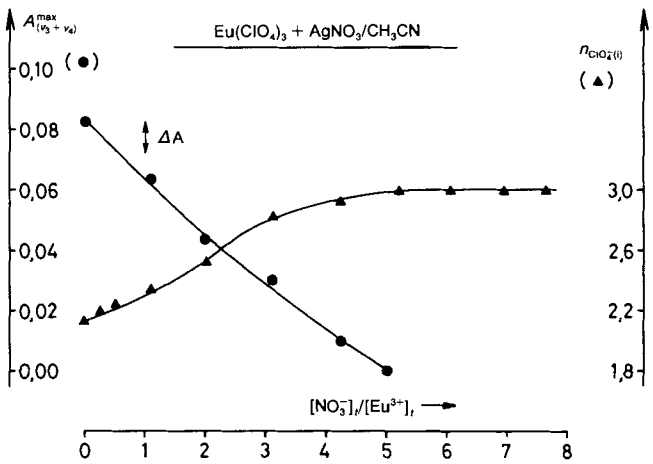

Fig. 4. *Variation of the average number of bonded perchlorate ions per Eu^{3+} ion and of the absorbance ($\nu_3 + \nu_4$) of bonded MeCN molecules* vs. $R = [NO_3^-]_t/[Eu^{3+}]_t$

$M_2[Ln(NO_3)_5]$ ($M = R_4N^+$). It is noteworthy that for $R = 5$, the absorption bands of the bonded NO_3^- ions are symmetrical and, therefore, comprised of one component only (for Nd, some asymmetry is observed, but the curve analysis indicates that an eventual second component represents only 2% of the total band area). This substantiates our choice to interpret the components of the nitrate vibrations in terms of nitrate inequivalences. The variation of the average $\tilde{\nu}_1 - \tilde{\nu}_4$ splitting *vs.* R is represented on *Fig. 5* for La and Yb. For both studied ions, the splitting decreases with increasing R's, which may be interpreted as reflecting a lengthening in the lanthanide–nitrate distances, when more nitrate ions are coordinated. Moreover, the increase in the mean $\tilde{\nu}_1 - \tilde{\nu}_4$ splitting *vs.* Z (*Table 5*) points to a growing Ln-nitrate interaction with increasing Z (electrostatic effect).

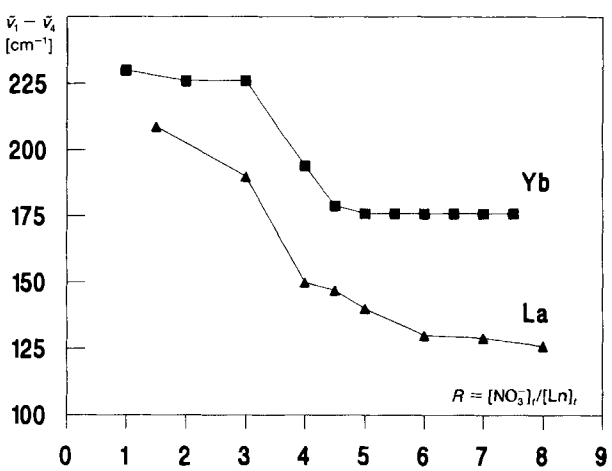

Fig. 5. *Average $\tilde{\nu}_1 - \tilde{\nu}_4$ splitting for $Ln(ClO_4)_3$ solutions 0.05 M in MeCN, containing nitrate, as a function of* $R = [NO_3^-]_t/[Ln]_t$

Table 5. *Curve Analysis of the ν_4 and ν_6 Vibrations of Coordinated Nitrate for $Ln(ClO_4)_3$ Solutions 0.05 M in Anhydrous MeCN Containing Nitrate*[a])

Ln^{III}	R	ν_4 [cm^{-1}]	s	ν_6 [cm^{-1}]	s
La	1.5	1288	1.5	817	1.5
	3.0	1300	2.6	819	3.0
		1286	0.4		
	4.0	1323	1.1	821	1.3
		1301	2.9	819	2.7
	5.0	1324	3.4	822	3.0
		1299	1.6	820	2.0
Nd	1.0	1292	0.3	818	0.4
		1278	0.7	814	0.6
	2.0	1300	1.0	818	0.9
		1281	1.0	815	1.1
	3.0	1304	1.9	818	2.2
		1287	1.1	816	0.8
	4.3	1304	4.3	818	4.3
	5.0	1324	0.1	819	5.0
		1305	4.9		
Eu	1.1	1282	1.1	813	1.1
	2.0	1301	0.5	815	1.0
		1282	1.5	813	1.0
	3.1	1311	1.3	818	1.0
		1294	0.9	816	0.8
		1281	0.9	814	1.3
	4.2	1310	3.3	818	2.4
		1291	0.9	815	1.8
	5.0	1310	5.0	818	5.0
Tb	1.3	1283	1.3	813	1.3
	2.8	1310	0.5	816	0.7
		1292	1.1	814	2.1
		1281	1.2		
	3.8	1312	2.3	818	1.2
		1293	0.9	816	1.0
		1281	0.6	814	1.6
	5.0	1311	5.0	817	5.0
Er	1.0	1288	1.0	813	1.0
	1.7	1294	0.7	814	0.7
		1284	1.0	813	1.0
	3.0	1296	1.7	815	1.3
		1285	1.3	813	1.7
	3.9	1317	2.0	818	1.4
		1296	1.1	816	1.2
		1285	0.8	814	1.3
	5.0	1317	5.0	817	5.0
Yb	1.0	1291	1.0	814	1.0
	2.0	1299	1.1	815	2.0
		1289	0.9		
	3.0	1302	1.4	815	3.0
		1290	1.6		
	4.0	1319	1.9	816	4.0
		1295	2.1		
	5.0	1319	4.5	817	5.0
		1295	0.5		

[a]) s is the relative band area (total band area = 3.0); $\Sigma\Delta^2$ is the goodness-of-fit parameter; $R = [NO_3^-]_t/[Ln]_t$.

The curve analysis of the ν_4 and ν_6 vibrations is given in *Table 5* (the ν_2 mode interferes with a perchlorate vibration). These results confirm the existence of nitrate inequivalences for $R > 1$, especially for the lanthanides in the middle of the series. A detailed analysis of the $\nu_1(NO_3^-$, bonded) vibration bandshape was performed for the $Yb(ClO_4)_3 + R\,AgNO_3$ system as a function of R, despite the interference mentioned above. The ν_1 vibration can be decomposed into two main components displaying bathochromic shifts with increasing R. For $R = 1$–3, the relative intensity of the lowest energy (internal) component of the ν_1 vibration remains constant, and then increases. This means that the number of NO_3^- ions bonded at longer distances from the Ln cation increases with R. A schematic representation of the various nitrato species is given on *Fig. 2*.

Coordination Numbers. The calculation of coordination numbers for the trinitrate solutions requires the knowledge of the number of coordinated solvent molecules which, in turn, requires the determination of the molar absorption coefficients ε of the bonded MeCN molecules. It was not possible to measure the ε's with a sufficient accuracy. However, an estimate of the CN's could be made, based on two assumptions: the ε's and the coordination numbers are the same for the nitrate and perchlorate solutions. The first hypothesis is acceptable, the observed shifts upon MeCN complexation being the same for perchlorate [12] and nitrate solutions. The second assumption is less reliable; however, we do not expect a large difference in CN's: slightly larger CN's were observed for nitrate solutions (0.5 unit on average) than for perchlorate solutions in presence of dimethylsulfoxide [11] [13]. Calculations performed for Nd, Eu, Tb, and Er yield CN = 9.0, 9.1, 8.3, and 8.2, respectively (±0.3).

The ν_1 and ν_6 vibrations were monitored in order to determine the average number of bonded NO_3^- ions per lanthanide, when nitrate is added to perchlorate solutions. This choice was made for the following reasons: *i*) the ν_4 vibration at 1295 cm^{-1} interferes with the Ag-bonded nitrate vibration (1302 cm^{-1}) for large values of R; *ii*) the ν_2 (1030 cm^{-1}) and ν_3 (735 cm^{-1}) vibrations appear in a spectral range, where solvent compensation is difficult to achieve; *iii*) ν_2 interferes with an absorption band of bonded ClO_4^- for $R < 4$. As nitrate absorption bands have several components, the values of the total areas $\int A\,d\tilde{\nu}$ have been plotted *vs.* R. A linear variation is observed up $R = 5$ for all lanthanide ions, followed by a constant value for $R > 5$ (*Fig. 6*). The intercept of the two straight segments allows one to calculate the coordination numbers: 9.8, 10.2, 10.0, 9.8, 9.9, and 9.9 for La, Nd, Eu, Tb, Er, and Yb, respectively. This determination was checked by the method of corresponding solutions [27] for Eu. The ν_6 vibration was analyzed for two solutions with $R = 6.95$, $[Eu]_t = 0.054$M and $R = 7.62$, $[Eu]_t = 0.081$M: the calculated CN was 10.0±0.3. Therefore, the addition of an excess nitrate leads to the formation of ten-coordinate species $[Ln(NO_3)_5]^{2-}$ exclusively. No hexanitrato species is observed, even for La. This is consistent with a similar observation by *Walker* and *Weeden* for Nd [21]. There is no decrease in CN for heavier ions, a fact which was verified by measuring the FT-IR spectrum of a 0.05M solution of $(Bu_4N)_2Yb(NO_3)_5$: no absorption band due to ionic nitrate is observed. The same constancy in CN prevails for the solid pentanitrates which all contain five bidentate nitrates: Ln = Ce [28], Eu [29], Ho [30], and Er [31]. The decrease in the Ln–O bond length in the series, *ca.* 2.57 Å (Ce), 2.48 Å (Eu), 2.45 Å (Ho) parallels the increasing $\tilde{\nu}_1 - \tilde{\nu}_4$ splitting in solution for $R = 5$, from 140 cm^{-1} (La) to ~ 180 cm^{-1} (Nd–Yb), and substantiate our simple explanation (*cf. Fig. 2*).

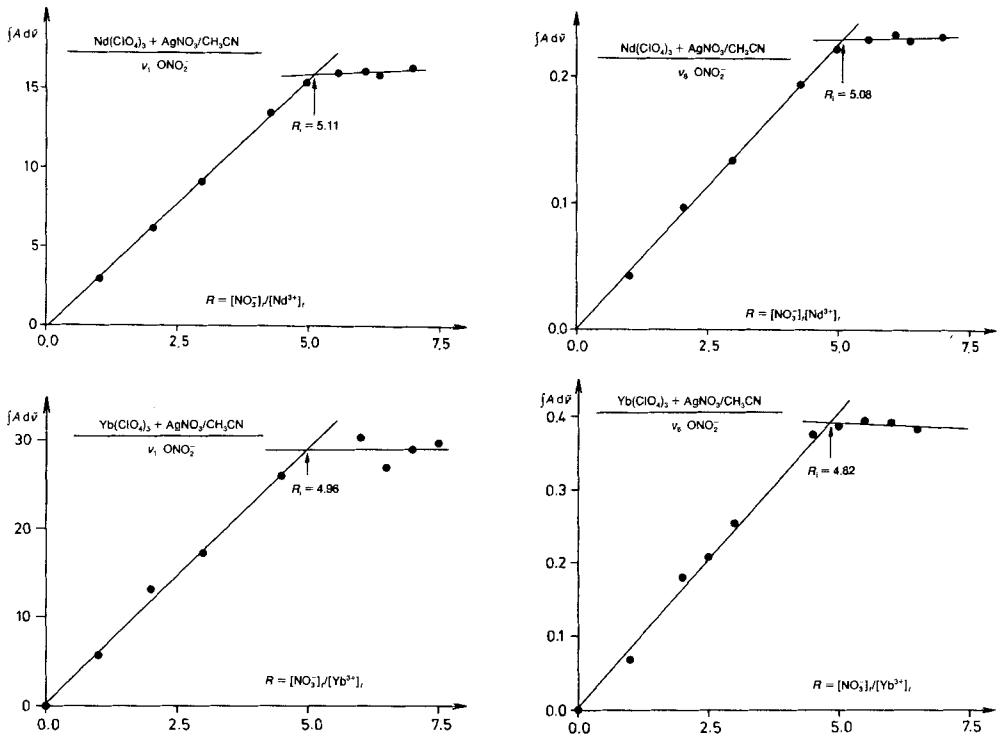

Fig. 6. *Total areas of the vibrations ν_1 and ν_6* vs. $R = [NO_3^-]_t/[Ln]_t$ *in solutions of* $Ln(ClO_4)_3$ *0.05* M *in anhydrous MeCN containing increasing amounts of nitrate*

Conclusion. – The above data show that bidentate nitrate ions in $[Ln(NO_3)_n]^{(3-n)+}$ species are not equivalent in solution, except when $n = 1$ and 5. The inequivalences vary with the atomic number of the lanthanide ion and are larger in the middle of the series. Moreover, if the average coordination number decreases with Z for the trinitrates, it remains constant in presence of an excess of nitrate (9.9±0.3). This and other work [10–13] point to a large variation of the coordination numbers with both the nature of the ligands bonded in the inner coordination sphere, the nature of the lanthanide ion, and the composition of the solutions. The inner coordination sphere of the lanthanide ions is, therefore, easily adjustable to the environment in which these ions are exposed. Henceforth, the versatility and adaptability of these elements when encompassed in many compounds, including organometallic molecules, or when they are used as spectroscopic probes in complex biological or environmental systems.

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