

FT-IR and fluorometric investigation of rare-earth and metal ion solvation

Part 10. Inner-sphere interaction between perchlorate and lanthanide ions in anhydrous acetonitrile*

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Abstract

The interaction between perchlorate and Ln(III) ions has been investigated in anhydrous acetonitrile for Ln = La, Pr, Sm, Gd, Dy, Ho, Tm and Yb. Control experiments have been carried out with Ln = Nd, Eu and Er. Vibrations assigned to unassociated (u), monodentate (m) and bidentate (b) perchlorate anions were identified in 0.05 M solutions of $\text{Ln}(\text{ClO}_4)_3$. Quantitative FT-IR measurements allowed the determination of the number of uncoordinated perchlorate ions, $\text{ClO}_4^-(\text{u})$, per Ln(III) ion, n_u , which increases from 1.43 (La) to 1.8–1.9 (Pr–Gd) and to 2.0–2.1 (Tb–Yb). Examination of other parameters such as the value and the variation of the $\nu_4(\text{E})-\nu_1(\text{A}_1)$ and $\nu_8(\text{B}_2)-\nu_1(\text{A}_1)$ splittings for $\text{ClO}_4^-(\text{m})$ and $\text{ClO}_4^-(\text{b})$ ions, respectively, the area of vibrational bands assigned to $\text{ClO}_4^-(\text{m})$, and the hypsochromic shift of vibrations assigned to bonded acetonitrile molecules, leads to the following interpretation. Both $\text{ClO}_4^-(\text{m})$ and $\text{ClO}_4^-(\text{b})$ ions are in the inner coordination sphere and the quantitative data point to a complicated situation in which several equilibria take place between species differing by the number of coordinated perchlorate ions, by the coordination mode of the perchlorate ions, and, probably, by the number of coordinated acetonitrile molecules. Changes in the average coordination number of the Ln(III) ions occur between La and Pr and at Gd. The equilibrium ratios for the formation of the monoperchlorato species could be evaluated for the heavier lanthanides: $\log K_1$ ranges between 1.8 and 2.7. Water molecules replace bonded perchlorate ions in the inner coordination sphere and so do chloride ions. The affinity of Ln(III) ions for chloride ions relative to perchlorate ions has been calculated to be $\log K_{\text{Cl}/\text{ClO}_4} = 1.1, 1.2$ and 0.5 for La, Nd and Er, respectively. Finally, an estimate of the formation constant of the monochloro complex of Er yielded $\log K_{\text{Cl}} = 2.6 \pm 0.7$.

Introduction

Owing to their large charge density and lack of directionality in chemical bonding, the trivalent lanthanide ions Ln(III) are highly solvated cations. In water, the average hydration number decreases from 9 for the lighter lanthanides to 8 for the heavier ones [1, 2]. Coordination numbers ranging from 10 to 8 have been reported for non-aqueous solutions. These numbers are often fractional, reflecting the presence of equilibria between differently solvated species. Changes in coordination number occur along the series and with the solvent composition. For instance, the interaction between lanthanide nitrates

and dimethyl sulfoxide has been recently studied in anhydrous acetonitrile [3]; the coordination number clearly depends upon the dimethyl sulfoxide concentration, increasing by approximately 0.5 unit when the ratio $[\text{DMSO}]/[\text{Ln(III)}]$ is increased from 3 to 6. In the absence of water, weakly coordinating anions such as perchlorate or triflate interact with lanthanide ions to form inner sphere complexes [4]. The presence of these species has been confirmed by FT-IR spectroscopy for Ln = Nd, Eu, Tb and Er [5, 6] in anhydrous acetonitrile, and by ^{139}La NMR measurements for La in methanol [7]. The interaction remains moderate and steric and electrostatic effects appear to be of the same order of magnitude. In this communication, we extend our previous study [5, 6] to most of the remaining members of the Ln

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series, namely La, Pr, Sm, Gd, Dy, Ho, Tm and Yb. We also discuss the apparent formation constants for the monoperchlorato species, $[\text{Ln}(\text{ClO}_4)]^{2+}_{\text{solv}}$ and investigate the influence of added chloride ions and water.

Experimental

Synthesis of the salts and preparation of the solutions

The hydrated perchlorates were prepared from the oxides (99.9 or 99.99%, Research Chemicals or Apache Chemicals) and reagent grade perchloric acid (Merck). Complete dehydration was achieved in two steps: (i) the salts were predried several days under vacuum (10^{-1} mmHg) in a desiccator containing NaOH, and (ii) the partially dehydrated salts were carefully heated under high vacuum at 50, 80 and 110 °C, until the pressure reached 10^{-5} mmHg. Analytical grade silver perchlorate (Merck) was used after drying at 90–110 °C. **Caution:** anhydrous perchlorates are highly explosive materials and any contamination by organic impurities or mechanical shock must be avoided! All samples were handled in water-free atmosphere (dry N_2 or Ar containing less than 10 ppm water) and were stored in sealed ampullas. Absence of water was checked by FT-IR spectroscopy. Tetraethylammonium chloride (Fluka, puriss) was dried 3–4 days at 50 °C under high vacuum (10^{-5} mmHg). Acetonitrile (Fluka) was treated with CaH_2 and P_4O_{10} , distilled twice and stored over 3 Å molecular sieves. The solutions, 0.05 M in Ln(III), were prepared under water-free atmosphere with the help of Metrohm E457 micropipettes, filtered, and their water content was determined by Karl Fischer titration (Mettler DL-18): they contained less than 0.3 mol H_2O per mol Ln(III). The lanthanide ion concentration was determined by complexometric analysis with Titriplex III (Merck) in the presence of urotropin and xylene-orange.

Infrared measurements

The FT-IR spectra were measured under nitrogen purge with a Bruker IFS 113v spectrometer equipped with a MCT photoconductive detector cooled to 77 K. The signal-to-noise ratios at 2000 cm^{-1} were 590 for 32 scans and 1500 for 256 scans. Solutions were introduced into specially designed Teflon® cells with a nominal optical path of either 23 or 50 μm . The actual optical path was determined before each experiment using the method of the interference fringes [7]. The cells were fitted with AgCl windows. This material creates some modulation of the baseline owing to its large refractive index; it was never-

theless chosen because perchlorates do not absorb on its surface. To avoid reaction with the solvent, Teflon®-coated O-rings were used to seal the cells. Interferograms were recorded with a 1-cm^{-1} band-pass (250–400 scans) and a 4-point apodization function was applied prior to the Fourier transformation. All the spectra were corrected for an optical path-length of 23 μm and when quantitative analysis was performed, the absorbances were corrected for the full width at half height (fwhh) of the investigated transition. Difference spectra were obtained in the following way. The solvent and solution spectra were recorded separately, but under the same experimental conditions, ratioed against the background, and transformed into absorbance units. The solvent spectrum was then numerically subtracted from the solution spectra with a different coefficient for each spectral range. The calibration curve for determining the concentration of unassociated perchlorate in solution was established with silver perchlorate (0.02–0.2 M) and found to be perfectly linear; the molar absorption coefficient of the band at 1100 cm^{-1} was $2270 \pm 35\text{ l mol}^{-1}\text{ cm}^{-1}$ for a fwhh of 24.5 cm^{-1} . Quantitative data reported in this paper are averages of 2–4 measurements on independently prepared solutions.

Results and discussion

Experimental facts

The difference spectra of $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile are partly reported in Fig. 1. Beside the two IR-active modes of unassociated perchlorate (u, symmetry T_d) one observes small absorption bands which can be assigned to monodentate (m, C_{3v}) and to bidentate (b, C_{2v}) perchlorate moieties. The investigated solutions being sufficiently dilute, we exclude the presence of bridging perchlorate in our assignments, especially that no vibration is observed at 1300 cm^{-1} . Such a vibration is typical of either a tridentate or a bridging perchlorate anion, as reported for solid copper, cobalt and nickel perchlorates [8]. The main absorption bands of the three ClO_4^- species are reported in Table 1. Some vibrational modes are missing because they interfere either with solvent vibrations or with other ClO_4^- modes. A complete assignment can only be done after mathematically decomposing the spectra into their components, as has been performed for Nd, Eu, Tb and Er [6]. When the symmetry of the uncoordinated perchlorate is lowered from T_d to C_{3v} upon monodentate coordination to the metal ion, the $\nu_3(T_2)$ vibrational mode at 1100 cm^{-1} is split into two components: $\nu_1(A_1)$ around 1030 cm^{-1} and $\nu_4(E)$ around $1155\text{--}1160\text{ cm}^{-1}$. The magnitude

TABLE 1. Main IR data (cm^{-1}) for perchlorate ions in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile^a

Assignment			Lanthanide							
u	m	b	La	Pr	Sm	Gd	Dy	Ho	Tm	Yb
	ν_8		1193	1199	1201	1198	1199	1200	na	na
		ν_4	1156	1157	1157	1155	1163	1163	1168	1168
ν_3			1102	1102	1102	1102	1102	1102	1102	1102
		ν_1	1028	1032	1032	1038	1038	1034	1028	1028
	ν_1		999	1000	999	1001	na	na	na	na
		ν_2	932	934	935	937	937	938	939	940
		ν_3	648	651	652	653	655	656	na	659
ν_4			625	625	625	625	625	625	625	625

^aAssignments from refs. 5 and 6; u=unassociated, m=monodentate, b=bidentate, na=not available without spectral decomposition.

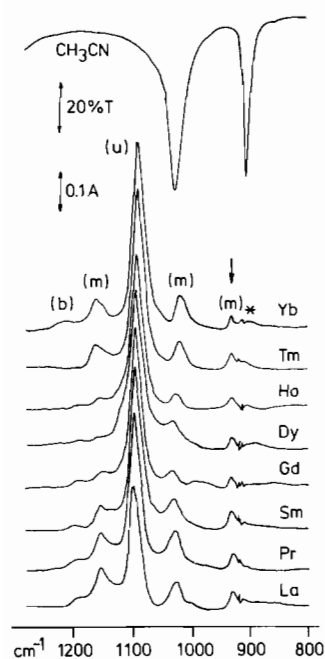


Fig. 1. Difference spectra of $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile, in the spectral range of the main perchlorate vibration. The arrow points to absorption from the coordinated solvent. Stars denote solvent absorptions that could not be completely compensated. Key: u=unassociated, m=monodentate, b=bidentate.

of the $\nu_4(\text{E})-\nu_1(\text{A}_1)$ splitting is therefore indicative of the strength of the $\text{Ln}(\text{III})/\text{ClO}_4^-$ interaction. The splitting ranges from 128 to 140 cm^{-1} and is close to the values reported for inner-sphere complexes, e.g. 134, 135 and 128 cm^{-1} for solid samples of $\text{Yb}(\text{HMPA})_4(\text{ClO}_4)_3$ [10], $\text{Fe}(\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ [11]. The trend along the lanthanide series is shown in Fig. 2. There is a slow decrease in the strength of the $\text{Ln}(\text{III})/\text{ClO}_4^-$ interaction from La(III) to Gd(III), followed by a steep increase up to Tm(III). In the case of bidentate

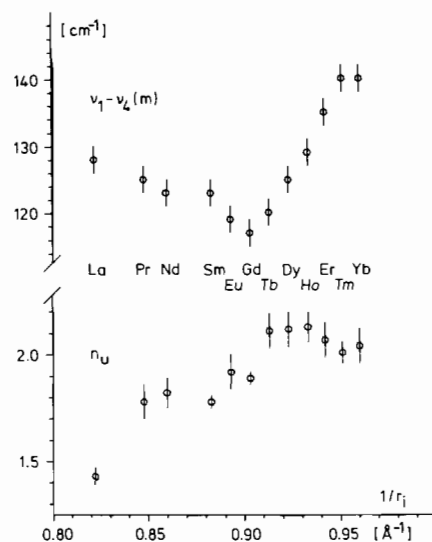


Fig. 2. Splitting $\nu_4-\nu_1$ (cm^{-1}) of monodentate perchlorate (top) and average number of coordinated perchlorate ions per $\text{Ln}(\text{III})$ ions, n_c (bottom), in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile vs. the reciprocal of the ionic radii [9] for a coordination number of 9. Data for Nd, Eu, Tb and Er have been remeasured and are slightly different from those reported in ref. 6.

coordination, the $\nu_3(\text{T}_2)$ vibration is split into three components $\nu_1(\text{A}_1)$, $\nu_6(\text{B}_1)$ and $\nu_8(\text{B}_2)$ around 1000, 1140 and 1200 cm^{-1} , respectively. Again, the $\nu_8(\text{B}_2)-\nu_1(\text{A}_1)$ splitting reflects the intensity of the $\text{Ln}(\text{III})/\text{ClO}_4^-$ interaction. The values we find are within the range 194–206 cm^{-1} , with no simple trend along the series. A splitting of 240 cm^{-1} is reported for anhydrous $\text{Cu}(\text{ClO}_4)_2$ while the estimated value for outer-sphere interaction is 50 cm^{-1} (*vide infra*). These data clearly point to both $\text{ClO}_4^-(\text{m})$ and $\text{ClO}_4^-(\text{b})$ being bonded into the first coordination sphere of the $\text{Ln}(\text{III})$ ions.

We have determined the concentration of $\text{ClO}_4^-(\text{u})$ in all the investigated solutions by using

the ν_3 absorption band and a calibration curve based on silver perchlorate solutions which are known to contain unassociated perchlorate only [5]. The results are presented in Table 2 while the variation of the average number of uncoordinated perchlorates per Ln(III) ions, n_u , is depicted in Fig. 2. The lanthanides can be divided into three groups: La, Pr–Gd and Tb–Yb for which $48 \pm 1\%$, $61 \pm 2\%$ and $69 \pm 2\%$ of the perchlorate anions are uncoordinated, respectively. The relative concentrations of ClO_4^- (m) and ClO_4^- (b) have not been determined, but we have shown for Nd, Eu, Tb and Er [6] that ClO_4^- (b) represents 15–30% of the total concentration of coordinated perchlorate ions. To get more insight into the nature of the Ln/ ClO_4^- interaction, we have measured the band area of two ClO_4^- (m) vibrations, ν_1 (m) and ν_4 (m). Both areas first decrease with increasing atomic number and then increase again (Fig. 3), but surprisingly the break occurs at Dy and not Gd, as could be expected from the data of Fig. 2.

Acetonitrile molecules bound to the Ln(III) ions give rise to distinct IR absorptions shifted towards higher energies. Two of these vibrations, ν_2 and

TABLE 2. Average number of unassociated perchlorates per Ln(III) ions, n_u , in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile

Ln	n_u	Reference	Ln	n_u	Reference
La	1.43 ± 0.04	a	Tb	2.11 ± 0.08	6
Pr	1.78 ± 0.08	a	Dy	2.12 ± 0.08	a
Nd	1.82 ± 0.07	6	Ho	2.13 ± 0.07	a
Sm	1.78 ± 0.03	a	Er	2.07 ± 0.08	6
Eu	2.08 ± 0.08	6	Tm	2.02 ± 0.05	a
	1.92 ± 0.08	a	Yb	2.04 ± 0.08	a
Gd	1.89 ± 0.03	a			

*This work.

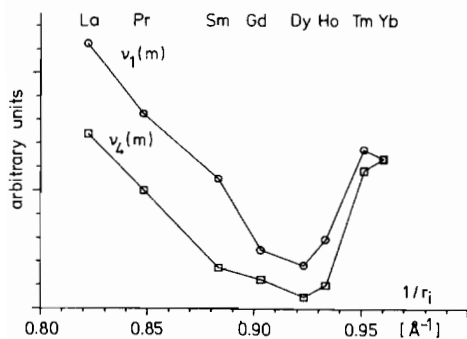


Fig. 3. Integrated band area of the ν_1 (m) (top) and ν_4 (m) (bottom) vibrations of monodentate perchlorate in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile vs. the reciprocal of the ionic radii [9] for a coordination number of 9.

$\nu_3 + \nu_4$, occur in the spectral range 2280 to 2320 cm^{-1} and are convenient to study (Fig. 4). The hypsochromic shifts range from 25 (La) to 34 (Yb) cm^{-1} for ν_2 and from 15 (La) to 22 (Yb) cm^{-1} for the combination, and their variation along the lanthanide series is linear (Fig. 5). This points to a monotonically increasing Ln/ CH_3CN interaction with the increase in electronic density of the ions, hence to a predominance of the electronic effects on the steric effects. It is noteworthy that the band area of ν_2 remains constant over the lanthanide series, indicating that the average number of coordinated acetonitrile molecules does not vary substantially from La to Yb. The band area of the combination $\nu_3 + \nu_4$ increases by c. 20–25% from La to Yb, but interpretation of these data is not easy since the intensity of a combination band is extremely sensitive to small changes in the force constants of the chemical bonds.

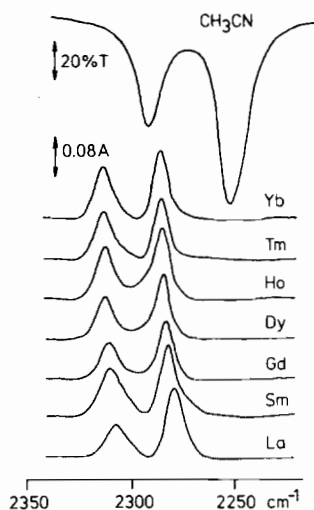


Fig. 4. Acetonitrile vibrations ν_2 and $\nu_3 + \nu_4$ in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile.

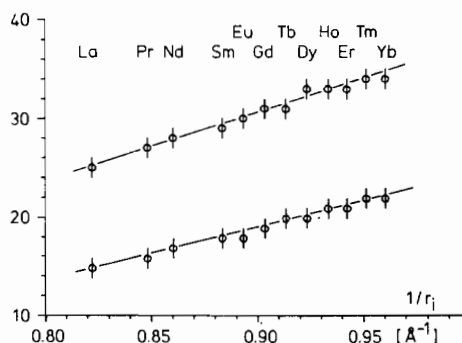
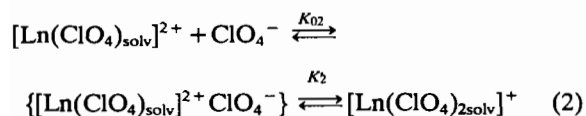
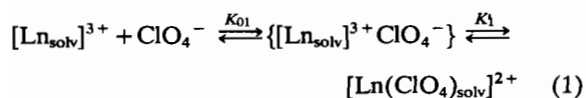


Fig. 5. Hypsochromic shift of the ν_2 (top) and $\nu_3 + \nu_4$ (bottom) vibrations of bonded acetonitrile molecules in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile.

Another experimental fact is of importance. We have observed that lanthanide perchlorate solutions containing more water than those for which data are reported above systematically display a less intense $\nu_3(u)$ vibration. We have therefore studied the influence of added water on $\text{Sm}(\text{ClO}_4)_3$ solutions. The range of water concentration investigated was 0.005–0.258 M, corresponding to ratios $R = [\text{H}_2\text{O}]/[\text{Sm}(\text{III})]$ varying from 0.1 to 5. The concentration of both $\text{ClO}_4^-(m)$ and $\text{ClO}_4^-(b)$ decreases upon water addition, pointing to water expelling perchlorate ions out of the first coordination sphere. On the other hand, the intensity of the $\nu_3(u)$ vibration, corrected for its fwhh, decreases by *c.* 20% when R is increased from 0.1 to 5. Control experiments have been carried out with AgClO_4 solutions containing the same concentrations of water: no variation in the intensity of $\nu_3(u)$ occurs, which precludes that the variation observed with $\text{Sm}(\text{III})$ solutions arises from an interaction between $\text{ClO}_4^-(u)$ and water. In fact the $\nu_3(u)$ absorption band in the solution with $R=5$ displays two shoulders at *c.* 1120 and 1075 cm^{-1} , which could correspond to the absorption of a monodentate species in the outer coordination sphere, with a $\nu_4(E)-\nu_1(A_1)$ splitting of *c.* 50 cm^{-1} .

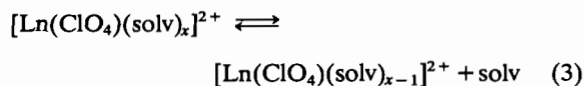
Interpretation

To rationalize our data with respect to the $\text{Ln}(\text{III})/\text{ClO}_4^-$ interaction, we consider the following simplified equilibria, disregarding the coordination mode of the perchlorate anions in the inner coordination sphere (monodentate or bidentate).



The variation of n_u along the series (Fig. 2 (bottom)) can be interpreted as reflecting the gradual displacement of the above equilibria towards the left. The change of both n_u and the $\nu_4-\nu_1$ splitting (Fig. 2 (top)) with increasing atomic number displays a break at Gd. In addition, the change of n_u with Z exhibits a discontinuity between La and Pr. This is consistent with the simple following interpretation taking into account both steric factors and the increase in electronic density with decreasing ionic radius. For La, the solution contains approximately 1/4 bis(perchlorato) species and 3/4 monoperchlorato complex. The proportion of the former decreases drastically for Pr (to *c.* 10%), then remains approximately constant until the middle of the series

and finally vanishes for Tb. Steric effects cause a lengthening in the Ln–ligand distance and as a result, the $\nu_4-\nu_1$ splitting decreases, despite the increasing electron density. The difference between La and Pr is not really a coordination number change, but rather the displacement of an equilibrium between two differently coordinated species. However, since we speak in terms of average coordination numbers, we may describe this change as reflecting a CN change of *c.* 0.5 unit. The discontinuities occurring at Gd may be interpreted as reflecting the displacement of an equilibrium involving two species differing by the number of coordinated acetonitrile molecules.



This is not in contradiction with the near constancy observed in the area of the $\nu_2(\text{CH}_3\text{CN})$ vibration versus Z . Indeed, a variation of one unit in x will cause a 10–12% variation in the band area and our accuracy on these data is ± 5 –8%. Moreover, the data of Fig. 3 may be understood by taking into consideration that the total band area of a vibrational band is proportional both to the concentration of the species and to the variation in dipole moment of the chemical bond. The latter variation will therefore increase with increasing $\text{Ln}(\text{III})/\text{ClO}_4^-$ interaction and the change in the area of both $\nu_1(m)$ and $\nu_4(m)$ results from the interplay of two converse factors, namely the decrease in $[\text{ClO}_4^-(m)]$ and the increase in the molar absorption coefficient, hence the break at Dy, rather than at Gd, in Fig. 3.

Returning to equilibrium (1), the relative concentrations of the solvated ion and of the monoperchlorato species present in the lanthanide solutions can be calculated from the data reported in Table 2 and from the total concentrations in $\text{Ln}(\text{III})$ and perchlorate ions. The apparent equilibrium quotients $K_1 = K_{01}K_1'$ may then be evaluated for the heavier lanthanide ions, under the assumption that the n_u values are not biased by outer-sphere perchlorate ions, two vibrations of which interfere with $\nu_3(u)$, *vide supra*. The values (Table 3) point to a

TABLE 3. Apparent equilibrium quotients for the formation of monoperchlorato species in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile (see text)^a

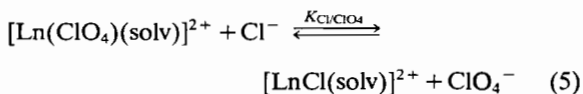
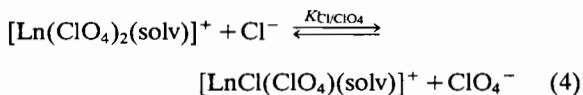
$\text{Ln}(\text{III})$	$\text{Log } K_1$ (l mol^{-1})	$\text{Ln}(\text{III})$	$\text{Log } K_1$ (l mol^{-1})
Tb	1.9 ± 0.4	Er	2.1 ± 0.4
Dy	1.8 ± 0.4	Tm	2.7 ± 0.5
Ho	1.8 ± 0.3	Yb	2.4 ± 0.4

^aData for Tb and Er are from ref. 6.

moderate interaction, with $\log K_1$ around 2. They are not precise enough to reveal differences along the series.

Effect of added chloride

To determine the relative complexation ability of chloride versus perchlorate for Ln(III) ions, we have added tetraethylammonium chloride to perchlorate solutions of La, Nd, Eu and Er. The concentration of uncoordinated perchlorate ions was determined as described above before and after the addition of chloride (Table 4). The experiment can be carried out with a small chloride concentration (0.04 to 0.05 M) only since lanthanide chloride complexes are sparingly soluble in anhydrous acetonitrile. Data clearly point to an increase in the concentration of unassociated perchlorate upon addition of chloride. Simultaneously, one observes a decrease in the intensity of the vibrational bands assigned to ClO_4^- (m) while the intensity of the bands assigned to coordinated acetonitrile molecules remains constant. Since the total chloride concentrations used are small and since the change in ClO_4^- (u) concentration is not large, we can interpret the data of Table 4 using the following simplified model which takes into account the presence of two new inner-sphere species only, the monochloro complex and a mixed chloro-perchlorato species, and which distinguishes two cases for light and heavy lanthanides, respectively.



Equation (4) could be applied to La and Nd and eqn. (5) to Er. Data for Eu do not yield consistent values of either K' or K , which means that a simplified

TABLE 4. Average number of unassociated perchlorates per Ln(III) ions, n_u , in $\text{Ln}(\text{ClO}_4)_3$ solutions (0.05 M) in anhydrous acetonitrile, without and with added chloride

Ln	$[\text{Ln(III)}]_t$ (l mol ⁻¹)	$[\text{Cl}^-]_t$ (l mol ⁻¹)	n_u^a	n_u^b
La	0.0490	0.0439	1.38 ± 0.08	1.85 ± 0.07
Nd	0.0537	0.0402	1.82 ± 0.04	1.98 ± 0.06
Eu	0.0524	0.0410	1.89 ± 0.10	2.12 ± 0.09
Er	0.0495	0.0533	2.08 ± 0.08	2.49 ± 0.08

^aWithout chloride; data are different from those listed in Table 2 because they have been evaluated from separate experiments (average of 4 solutions). ^bIn presence of chloride.

model cannot be used in this case. We find $\log K_{\text{Cl}/\text{ClO}_4} = 1.1 \pm 0.2$ for La and 1.2 ± 0.2 for Nd, and $\log K_{\text{Cl}/\text{ClO}_4} = 0.5 \pm 0.3$ for Er. Combining this latter value with $K_1(\text{Er})$ found for the formation of the monoperchlorato species, the apparent formation constant of the monochloro complex $[\text{ErCl}_{\text{sol}}]^{2+}$ is estimated to $\log K_{\text{Cl}} = 2.6 \pm 0.7$. In view of the assumptions made to calculate these constants, a strict comparison with literature data is not possible; we note, however, that Hamze *et al.* [12] report $\log K_{\text{Cl}}$ values ranging from 1.7 to 2.0 for Pr, Nd and Sm in propylene carbonate and that we have found $\log K_{\text{Cl}/\text{ClO}_4} = 0.6$ for La in methanol [4].

Conclusions

This study enlightens the fact that the Ln(III)/ ClO_4^- interaction in anhydrous acetonitrile results in equilibria involving, beside outer-sphere complexes, several different inner-sphere species which differ by the number of coordinated perchlorate ions, the coordination mode (monodentate or bidentate) and, probably, the number of coordinated acetonitrile molecules. They are two changes in the average coordination number, one between La and Pr and the other at Gd. A detailed quantitative analysis is not possible on the basis of the available data, but the equilibrium ratios for the formation of monoperchlorato species can be evaluated with the help of simplifying assumptions. The interaction is moderate ($\log K_1 = c. 2$) but is strong enough to be taken into account when interpreting stability constants determined in the presence of excess perchlorate as supporting electrolyte. Chloride is shown to be a better coordinating anion than perchlorate and the relative affinity for the former is larger in acetonitrile than in methanol.

Acknowledgements

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