reaction with $Fe(TMPyP)^{4+}$ suggests that an Fe(IV) species is not an intermediate.

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**Registry No.** $Fe(TMPyP)^{5+}$, 60489-13-6; $Fe(TMPyP)^{4+}$, 71794-64-4; $Fe(TMPyP)(OH)^{4+}$, 97889-58-2; $O_2$, 7782-44-7; $H_2O_2$, 7722-84-1; ascorbate, 50-81-7.

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# FT IR Investigation of the Interaction between Perchlorate and Trivalent Neodymium, Europium, Terbium, and Erbium Ions in Anhydrous Acetonitrile[1,2]

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The interaction between perchlorate and Nd(III), Eu(III), Tb(III), and Er(III) ions has been investigated in anhydrous $CH_3CN$ and $CD_3CN$. Vibrations due to unassociated (u), monodentate (m), and bidentate (b) perchlorate ions could be identified in 0.05 M solutions of $Ln(ClO_4)_3$. Quantitative FT IR measurements allowed the determination of the number of $ClO_4^-$(u) ions per Ln(III) ion, $n_u$, which is equal to 1.82 (Nd), 2.13 (Eu), 2.11 (Tb), and 2.07 (Er). This is in agreement with conductometric data that correspond to 2:1 electrolytes. The proportion of $ClO_4^-$(b) is low, between 5 and 10% of the total perchlorate concentration, whereas the proportion of $ClO_4^-$(m) varies from 39% (Nd) to ca. 22 ± 4% for Eu, Tb, and Er. The influence of the solvent on the concentration of the various perchlorate species has also been determined. For Eu, $n_u = 1.5$ in acetone and 2.4 in methanol. The proportion of $ClO_4^-$(b) is much lower in these two solvents than in acetonitrile. Inner-sphere $Ln(III)/ClO_4^-$ interactions consistent with these findings are proposed. Therefore, the data reported in this study indicate that the solutions contain the lanthanide species $[Ln_{solv}]^{3+}$, $[LnClO_4(m)_{solv}]^{2+}$, $[LnClO_4(b)_{solv}]^{2+}$, and $[Ln(ClO_4)_2(\text{m and/or b})_{solv}]^+$. Their concentrations are evaluated as well as the apparent equilibrium ratio for the monoperchlorato species: $\log K_1$ (±0.5) = 1.8, 1.9, and 2.1 for Ln = Eu, Tb, and Er. A difference is observed between the behavior of Nd(III) and that of the other Ln(III) ions included in this report.

## Introduction

Trivalent lanthanide complexes and solvates are dominated by strong ion–dipole interactions and therefore do not display the restricted stereochemistry typical of the d transition elements. The number and arrangement of the ligand donor atoms in the primary coordination sphere are the result of the interplay between steric and electrostatic factors,[4] and coordination numbers ranging from 3 to 14 have been reported in the solid state.[5,6] In solution, despite almost 3 decades of research, many aspects of the coordination chemistry of these metal ions remain unclear. In particular, the questions of an eventual coordination change within the 15-element series or of the exact bonding mode (i.e. inner or outer sphere) for specific ligands are still open. Since the lanthanide ions are being increasingly used as spectroscopic probes in biochemistry,[7,8] more basic information is needed. The field has been recently reviewed,[9,10] and the use of modern instrumentation has enabled the acquisition of valuable data, especially in water[11] and in aqueous organic solvents.[12,13] In previous parts of this series of papers, we have tried to determine the coordination numbers of some Ln(III) ions (Ln = Nd, Eu, Tb, Er) in anhydrous solutions of weakly coordinating organic solvents.[3,14–18] In particular, we have addressed the problem of perchlorate coordination to europium ion in acetonitrile solutions and were able to prove by FT IR spectrometry that some degree of inner-sphere coordination occurs.[14] In this paper, we extend our vibrational study to lighter (neodymium), intermediate (terbium), and heavier (erbium) lanthanide ions in order to investigate whether differences appear in their solution behavior when the ionic radius is varied. New data for europium perchlorate are also provided.

## Experimental Part

Lanthanide perchlorates were prepared from the 99.99% pure oxides (Glucydur) and reagent grade perchloric acid (Merck). Complete dehydration of the salts was performed at 60–110 °C, under reduced pressure, $10^{-5}$ mmHg, during 10–12 days. Analytical grade silver perchlorate (Merck) was used after drying at 90–110 °C. Acetonitrile (Fluka) and deuterated acetonitrile (99.8%, Ciba-Geigy) were treated with $CaH_2$ and $P_4O_{10}$ and distilled. The solutions were prepared under a strictly controlled atmosphere of $N_2$, with less than 10 ppm water, and contained less than 0.1 molecule of water per Ln(III) ion. In a few cases, the solutions had to be filtered to eliminate traces of insoluble oxychlorides generated during the dehydration of the perchlorates. The lanthanide ion concentration was determined by complexometric analysis with Ti-

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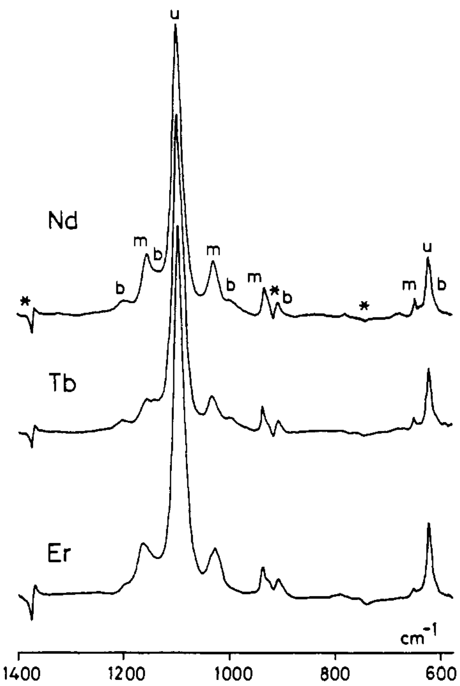

**Figure 1.** FT IR difference spectra of $Ln(ClO_4)_3$ 0.05 M in anhydrous $CH_3CN$. Asterisks denote solvent absorptions that cannot be completely compensated. Key: u = unassociated, m = monodentate, b = bidentate.

triplex III (Merck) in the presence of urotropin and xylene orange. The FT IR spectra were recorded on a Bruker IFS-113c spectrometer using special leak-proof liquid cells with silver chloride windows, according to the procedure previously described.[14]

All the reported data are averages of two to three measurements on independently prepared solutions, to minimize any error due to an eventual absorption of water. In the course of the investigations, two different detectors were used, a TGS pyroelectric detector and a MCT photoconductive detector. This latter is more sensitive but is known to be nonlinear,[19] with calibration being needed for quantitative measurements. This was performed with 12 absorption bands of acetonitrile; the mean deviation from the $\epsilon^{max}$ values reported by Jones et al.[20] was $2\sigma$ = 1.8% for the TGS detector, and correction factors have been worked out for the MCT detector after each realignment of the optical layout of the spectrometer. Deconvolutions of the spectra were done by using a Cauchy function to simulate the absorption line shape.[21]

## Results and Discussion

The IR spectra of anhydrous 0.05 M solutions of the lanthanide perchlorates studied in acetonitrile are presented in Figure 1. In addition to the two absorptions at 625 and 1100 cm$^{-1}$ assigned to unassociated perchlorate ions (u, symmetry $T_d$),[14] the spectra of these solutions display several other weak absorptions. A comparison of their wavenumbers with those reported in Hathaway's work[22] allows one to assign them to monodentate (m, $C_{3v}$) and bidentate (b, $C_{2v}$) perchlorate ions interacting with the metal ions. Solutions in deuterated acetonitrile were measured to better differentiate the bands between 900 and 950 cm$^{-1}$, and the spectra were deconvoluted in order to minimize interferences from the $ClO_4^-$(u) bands (Figure 2). In this way, the seven IR-active vibrational modes of $ClO_4^-$(b) and five of the six modes of $ClO_4^-$(m) could be identified (Table I); the sixth IR-active mode of the monodentate perchlorate occurs between 460 and 480 cm$^{-1}$ [22] and could not be measured with the MCT detector. The $\nu_3(T_2)$ and $\nu_4(T_2)$ vibrational modes of the unassociated perchlorate are split when the symmetry of the anion is lowered by association with the metal ion. Each $T_2$ mode is split into two components by monodentate association ($\nu_4$, $\nu_1$ and $\nu_3$, $\nu_5$) and into three

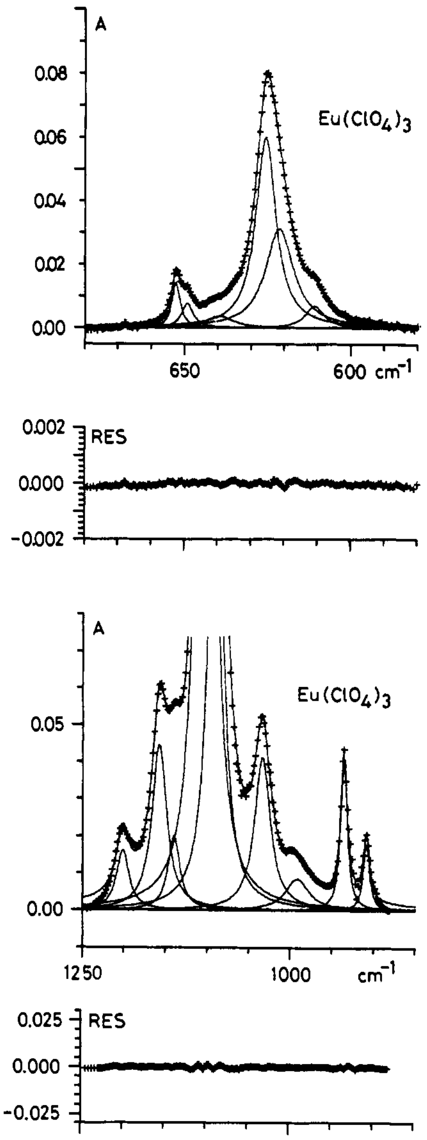

**Figure 2.** Deconvolution of the FT IR difference spectrum of a $Eu(ClO_4)_3$ solution 0.05 M in anhydrous $CH_3CN$, with residuals at the bottom.

**Table I.** IR Data (cm$^{-1}$) for Perchlorate Ions in $Ln(ClO_4)_3$ Solutions 0.05 M in Anhydrous $CH_3CN$[a]

| assignt[22] | | | | | | |
|---|---|---|---|---|---|---|
| u | b | m | Nd | Eu | Tb | Er |
| | $\nu_8$ | | 1198 w | 1201 w | 1198 w | 1199 w |
| | | $\nu_4$ | 1158 m | 1157 m | 1160 m | 1167 m |
| | | | | | | 1156 sh |
| | $\nu_6$ | | 1140 sh | 1140 sh | 1142 sh | 1143 sh |
| $\nu_3$ | | | 1102 vs | 1103 vs | 1102 vs | 1102 vs |
| | | | 1090 sh | 1090 sh | 1091 sh | 1092 sh |
| | | $\nu_1$ | 1030 s | 1029 m | 1029 m | 1026 m |
| | $\nu_1$ | | 992 w | 992 w | 995 w | 998 w |
| | | $\nu_2$ | 929 w | 931 w | 932 w | 928 w |
| | $\nu_2$ | | 909 w | 909 w | 908 w | 908 w |
| | | $\nu_3$ | 651 w | 653 w | 654 w | 655 w |
| | $\nu_3$ | | 648 sh | 649 sh | 651 sh | 652 sh |
| | $\nu_7$ | | 640 vw | 639 vw | | 643 vw |
| $\nu_4$ | | | 625 m | 626 m | 626 m | 626 m |
| | | $\nu_5$ | 620 sh | 611 sh | 622 sh | 622 sh |
| | $\nu_9$ | | 612 w | 611 w | 611 w | 614 w |
| $\nu_4 - \nu_1$ (m) | | | 128 (1) | 128 (1) | 131 (1) | 130 (1) |
| $\nu_3 - \nu_5$ (m) | | | 31 (1) | 32 (1) | 32 (1) | 33 (1) |
| $\nu_8 - \nu_1$ (b) | | | 206 (3) | 209 (3) | 203 (4) | 201 (4) |
| $\nu_3 - \nu_9$ (b) | | | 36 (1) | 38 (1) | 40 (1) | 40 (1) |

[a] From deconvoluted spectra. Key: vw, very weak; w, weak; m, medium; s, strong; sh, shoulder. Standard deviations are indicated in parentheses.

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**Table II.** Average Number of Unassociated Perchlorates per Ln(III) Ion, $n_u$, and Percentages of $ClO_4^-$(u), $ClO_4^-$(m), and $ClO_4^-$(b) in $Ln(ClO_4)_3$ Solutions ca. 0.05 M in Anhydrous $CH_3CN$ and $CD_3CN$

| Ln | $n_u$[a] | $n_u$[b] | $ClO_4^-$(u) | $ClO_4^-$(m) | $ClO_4^-$(b) |
|---|---|---|---|---|---|
| Nd | 1.82 ± 0.07 | 1.78 | 61 ± 2 | 39 ± 2 | 6 ± 2 |
| Eu | 2.13 ± 0.08 | 2.08 | 71 ± 3 | 19 ± 3 | 10 ± 2 |
| Tb | 2.11 ± 0.08 | 2.14 | 70 ± 3 | 20 ± 4 | 10 ± 2 |
| Er | 2.07 ± 0.08 | 2.02 | 69 ± 3 | 26 ± 4 | 5 ± 2 |

[a] Average of four determinations on $A^{max}(\nu_3)$ (TGS and MCT detectors). [b] One determination using the total band area ($\nu_3$).

components by bidentate association ($\nu_8$, $\nu_6$, $\nu_1$ and $\nu_3$, $\nu_7$, $\nu_9$). The energy differences $\nu_4 - \nu_1$ (m), $\nu_3 - \nu_5$ (m), $\nu_8 - \nu_1$ (b), and $\nu_3 - \nu_9$ (b) are related to the strength of the Ln(III)/$ClO_4^-$ interaction. The difference values reported in Table I do not show significant changes from one lanthanide ion to the other. It is noteworthy that the IR spectra do not contain any component in the 1300-$cm^{-1}$ region that could be assigned to tridentate or bridging perchlorate ions, as has been observed in the solid state for copper, cobalt, and nickel perchlorates.[23]

Conductometric measurements of $10^{-2}$ M lanthanide perchlorate solutions are in agreement with the presence of coordinated perchlorate in solution: $\Lambda_M$ is equal to 208 (Nd), 214 (Eu), 220 (Tb), and 214 (Er) $\Omega^{-1}\cdot cm^2\cdot M^{-1}$, which corresponds to 2:1 electrolytes.[24] We have determined the concentration of $ClO_4^-$(u) in these solutions with the help of calibration curves based on silver perchlorate solutions that contained unassociated perchlorate only.[14] The same results were obtained when either the absorbance at the maximum of the $\nu_3$ absorption band, $A^{max}(\nu_3)$ or the total band area was used to construct the calibration curves (Table II). These calibration curves are perfectly linear up to an absorbance of 0.6–0.7. The number of unassociated perchlorates per Ln(III) ion is close to 2 and therefore consistent with the conductometric data. This number is comparable for Eu, Tb, and Er but significantly smaller for Nd, suggesting either that steric effects may play an appreciable role in perchlorate coordination and partly counterbalance the increase of the electrostatic interaction in going from Nd to Eu or that the varying tendency of the metal ions to associate with solvent results in differences in the amount of associated $ClO_4^-$. In order to determine the concentrations of $ClO_4^-$(m) and $ClO_4^-$(b), we have added excess perchlorate to the solutions in $CH_3CN$ and $CD_3CN$. No additional absorption bands appeared, but the intensity of all the perchlorate bands increased with $R = [ClO_4^-]_t/[Ln(III)]_t$, where the subscript t indicates total concentrations. These variations are reported in Figure 3 for two vibrational modes of both monodentate and bidentate perchlorates. The concentration difference for the monodentate perchlorate between $R = 3$ and $R = 6$ is the largest for neodymium (28%) and then decreases with increasing $Z$ to reach 18% for erbium. The behavior of the concentration difference for the bidentate perchlorate between $R = 3$ and $R = 6$ is more complicated, being maximal for europium and terbium (ca. 32–39%) and minimal for neodymium and erbium (ca. 18–21%). An estimate of the absolute concentrations of the mono- and bidentate perchlorates has been done as follows. First, the total concentration of associated $ClO_4^-$ was calculated from [$ClO_4^-$(u)] and $[ClO_4^-]_t$. Then, the internal standard method proposed by Koenig[25] was applied. Two pairs of solutions in $CH_3CN$ and $CD_3CN$ with $R = 3$ and 4, that is having different concentrations of $ClO_4^-$(m) and $ClO_4^-$(b), were prepared. The intensities of the $\nu_2$ (m, $CD_3CN$), $\nu_3$ (m, $CH_3CN$) and $\nu_2$ (b, $CD_3CN$), $\nu_8$ (b, $CH_3CN$) absorptions were measured and introduced into the expression of Beer's law for a binary mixture. Since neither $ClO_4^-$(m) nor $ClO_4^-$(b) absorbs at wavenumbers at which the other associated species absorbs and since we have two pairs of solutions, it is possible to eliminate the molar absorption coefficients from the equations and to calculate the concentrations of $ClO_4^-$(m) and $ClO_4^-$(b). For the neodymium solutions, the total concentration of bound perchlorate exceeded the metal concentration and the proportion of metal under the form of bis(perchlorato) complexes amounted to 17 and 30% for $R = 3$ and 4, respectively. The number of bound perchlorate ions per metal ion was also larger than 1 for the other lanthanide solutions when $R$ was larger than four, but the presence of bis(perchlorato) complexes did not result in the appearance of new bands in the spectra. An examination of the percentages of the

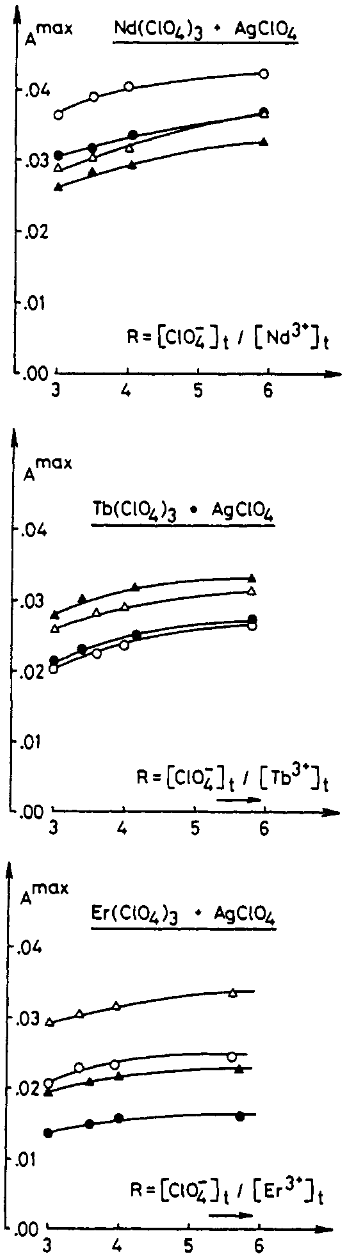

**Figure 3.** Absorbance variations of vibrational modes of associated perchlorate vs. perchlorate concentration: ▲ $\nu_8$ (b) and ● $\nu_3$ (m) in $CD_3CN$; △ $\nu_2$ (b) and ○ $\nu_2$ (m) in $CH_3CN$. The lanthanide ion concentration is ca. 0.05 M.

**Table III.** Relative Concentrations (%) of Perchlorato Complexes Present in Lanthanide Perchlorate Solutions ca. 0.05 M in Anhydrous Acetonitrile

| | | perchlorato complexes | |
|---|---|---|---|
| Ln | solvate | monodentate | bidentate |
| Nd | | 83[a] | 17[a] |
| Eu | 13 | 57 | 30 |
| Tb | 10 | 60 | 30 |
| Er | 7 | 78 | 15 |

[a] Presence of bis(perchlorato) complexes.

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**Table IV.** Acetonitrile Vibrations ($cm^{-1}$) in Anhydrous $Ln(ClO_4)_3$ Solutions 0.05 M[a]

| assignt | solvent | Nd | Eu | Tb | Er |
|---|---|---|---|---|---|
| $\nu_3 + \nu_4$ | $CH_3CN$ | 2310 (+17) | 2311 (+18) | 2313 (+20) | 2314 (+21) |
| $\nu_2$ | $CH_3CN$ | 2281 (+28) | 2283 (+30) | 2284 (+31) | 2286 (+33) |
|  | $CD_3CN$ | 2291 (+29) | 2296 (+33) | 2298 (+35) | 2300 (+37) |
| $\nu_4$ | $CH_3CN$ | 935 (+17) | 936 (+18) | 937 (+19) | 939 (+21) |
|  | $CD_3CN$ | 847 (+15) | 849 (+17) | 850 (+18) | 851 (+19) |
| $\nu_8$ | $CH_3CN$ | 397 (+19) | 398 (+20) | 401 (+23) | 402 (+24) |
|  | $CD_3CN$ | 367 (+19) | 369 (+21) | 370 (+22) | 372 (+24) |

[a] The shifts with respect to the bulk solvent are indicated between parentheses. The assignments are made on the basis of a $C_{3v}$ local symmetry.[33]

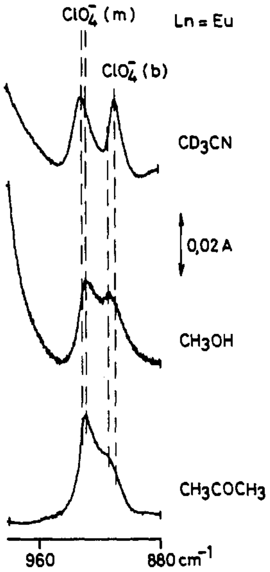

**Figure 4.** Part of the IR spectra of $Eu(ClO_4)_3$ 0.05 M in various solvents.

various perchlorate moieties present in solution for $R = 3$ (Table II) leads to two conclusions: (i) the proportion of $ClO_4^-$(m) is larger for Nd(III) than for the other Ln(III) ions, and (ii) the concentration of $ClO_4^-$(b) remains quite low for all the metal ions. We have also studied the influence of the solvent on the relative concentrations of the various perchlorate ions. The number of unassociated perchlorates per lanthanide ion is minimal in acetone ($n_u$ = 1.50 (15) for Eu) and maximal in methanol ($n_u$ = 2.40 (15) for Nd, Eu, Er). These values are again in agreement with the conductometric data: $\Lambda_M$ = 90 and 170 $\Omega^{-1}\cdot cm^2\cdot M^{-1}$ for solutions in acetone and methanol, which approximately correspond to 1:1 and 2:1 electrolytes, respectively.[24] The behavior of the coordinated perchlorate ions was monitored by using bands between 900 and 950 $cm^{-1}$ that are assigned to $ClO_4^-$(m) and $ClO_4^-$(b) (Figure 4). The frequency of $\nu_2$ (m) is little affected by both the solvent and the lanthanide ion, whereas $\nu_2$ (b) is displaced from 909 $cm^{-1}$ in acetonitrile to 913 $cm^{-1}$ in methanol and to 916 $cm^{-1}$ in acetone. The proportion of $ClO_4^-$(b) with respect to the total perchlorate concentration has been determined by Koenig's method. It is not the same in the three solvents and for all the metal ions. In methanol, it decreases considerably in going from neodymium (7%) to erbium (2%). For europium, it varies from 10% in acetonitrile to 6% in acetone and 3% in methanol. The proportion of $ClO_4^-$(m) follows a reverse trend, increasing in methanol from 13% (Nd) to 18% (Er), and ranging, for europium, from 19% in acetonitrile to 44% in acetone and 17% in methanol. These results cannot be interpreted in a clear-cut manner, especially because the degree of association in acetone is much larger than would be expected from a simple consideration of the solvent donor properties: the donor numbers are 14.1, 17.0, and 19.0 for acetonitrile, acetone, and methanol, respectively.[26]

The question now arises whether the perchlorate interaction is inner or outer sphere. Evidences of inner-sphere complexes have been brought by both NMR and ultrasonic measurements. For instance, $^{35}$Cl NMR data on ytterbium perchlorate solutions in acetone/water mixtures have been interpreted as reflecting the presence of mono-, bis-, and tris(perchlorato) inner-sphere complexes.[27] Moreover, ultrasonic absorption experiments point to the simultaneous presence of inner- and outer-sphere perchlorates in methanolic solutions of Nd, Gd, and Er perchlorates.[28]

The presence of inner-sphere complexes in the solutions we have investigated is suggested by the far-IR region of the spectra, where a broad band around 200–220 $cm^{-1}$ may be assigned to Ln–O vibrations by comparison with the spectra of lanthanide nitrate solutions. We could therefore rationalize our results in two ways: (i) both $ClO_4^-$(m) and $ClO_4^-$(b) interact in the inner coordination sphere of the Ln(III) ions, or (ii) one of these species is outer sphere. Some arguments were given to substantiate this latter hypothesis.[14] However, considering that an outer-sphere interaction is likely to perturb the vibrational spectra only slightly and that the splittings of the $\nu_3(T_2)$ mode of the ionic perchlorate by both monodentate and bidentate association are large,[29] the first hypothesis seems to be more likely. Our results could then be rationalized considering the equilibria

$$[Ln_{solv}]^{3+} + ClO_4^- \xrightleftharpoons{K_{01}} \{[Ln_{solv}]^{3+}ClO_4^-\} \xrightleftharpoons{K'_1} [Ln(ClO_4)_{solv}]^{2+}$$

$$[Ln(ClO_4)_{solv}]^{2+} + ClO_4^- \xrightleftharpoons{K_{02}} \{[Ln(ClO_4)_{solv}]^{2+}ClO_4^-\} \xrightleftharpoons{K'_2} [Ln(ClO_4)_{2solv}]^{+}$$

$$[LnClO_4(m)_{solv}]^{2+} \xrightleftharpoons{K_{m/b}} [LnClO_4(b)_{solv}]^{2+}$$

The relative concentrations of the solvated ion and of the perchlorato species present in the lanthanide solutions may be calculated from the data reported in Table II and from the total lanthanide and perchlorate concentrations. They are listed in Table III. The apparent equilibrium quotients, $K_1 = K_{01}K'_1$, expressed in concentrations, may be deduced assuming the presence of mono(perchlorato) species only: log $K_1$ = 1.8 ± 0.5, 1.9 ± 0.5, and 2.1 ± 0.5 for Ln = Eu, Tb, and Er, respectively. For Ln = Nd, neither $K_1$ nor $K_2 = K_{02}K'_2$ can be evaluated, since we cannot determine the proportion of mono- and bis(perchlorato) complexes.

Acetonitrile molecules bound to the Ln(III) ions give rise to distinct IR absorptions that are shifted toward higher energies (Table IV). These absorptions display a hypsochromic shift with respect to the increasing atomic number of the lanthanide, pointing to an increasing $CH_3CN$/Ln(III) interaction. This may be understood in view of the small steric hindrance of the acetonitrile molecule. The observed shifts are similar to those reported for In(III):[30] 23 and 37 $cm^{-1}$ for $\nu_3 + \nu_4$ and $\nu_2$, respectively. The corresponding shifts for univalent cations, e.g. Ag(I)[14] and Tl(I),[30] are substantially smaller: 6–10 and 16–18 $cm^{-1}$, respectively. A quantitative determination of the number of bound acetonitrile molecules per metal ion cannot be made directly,[14] and a discussion of the coordination numbers of the lanthanide ions in these so-

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lutions will be presented in a subsequent paper.

### Conclusion

This study confirms that perchlorate ions form inner-sphere complexes with lanthanide ions in weakly to moderately coordinating solvents. Evidence for such complexes is still rare,[26,28] but their existence is being increasingly invoked, even in aqueous solutions. For instance, the decrease of the hydration number of the Lu(III) ion upon addition of an excess of perchlorate has been tentatively attributed to coordination of the perchlorate ion.[12] Similarly, the decrease in the lifetime of the $^5D_0$ excited state of the Eu(III) ion in aqueous perchlorate solutions upon addition of sodium perchlorate or upon an increase in concentration was explained by a change in the hydration number consecutive with the penetration of a perchlorate ion in the Ln(III) coordination sphere.[31,32] From the quantitative data that we report for anhydrous acetonitrile solutions, it appears that the Ln(III)/$ClO_4^-$ interaction remains moderate and that steric and electrostatic effects are of the same order of magnitude, which explains the larger concentration of associated perchlorate observed for the lighter neodymium ion. Finally, one notes that within the series of investigated ions the largest differences occur between Nd(III) and Eu(III), with most of the data for the intermediate and heavier ions being more or less equal within experimental error.

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**Registry No.** $Nd(ClO_4)_3$, 13498-06-1; $Eu(ClO_4)_3$, 13537-22-9; $Tb(ClO_4)_3$, 14014-09-6; $Er(ClO_4)_3$, 14017-55-1; MeCN, 75-05-8.

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# Characterization of the Binding, Kinetics, and Redox Stability of Vanadium(IV) and Vanadium(V) Protein Complexes in Serum

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The redox kinetics and complexation of vanadium(IV) and vanadium(V) with albumin and transferrin in serum and buffer solution were studied. $^{35}Cl$ and $^{14}N$ NMR line width measurements of chloride, perchlorate, and nitrate binding to transferrin, ultraviolet difference spectroscopy, equilibrium dialysis, and ultrafiltration experiments confirm that a specific 2:1 complex is formed between vanadium(V) and apotransferrin. In contrast, vanadium(V) binds only weakly to albumin. EPR data reveal the presence of reducing agents in fresh serum that quantitatively convert vanadate(V) to vanadyl(IV), resulting in formation of specific $VO^{2+}$–albumin and $(VO^{2+})_2$–transferrin complexes. Half-lives for air oxidation of vanadium(IV) albumin and transferrin complexes and for the reduction of vanadium(V) by endogenous reducing agents in serum fall in the range 5–30 min at pH 7.5. Thus, the interconversion between oxidation states is rapid relative to the normal residence time of vanadium in the circulation. The data suggest that the metal is probably present in both oxidation states in the bloodstream and that albumin as well as transferrin may be involved in the transport of vanadium(IV) whereas vanadium(V) is possibly carried by transferrin alone.

## Introduction

Interest in the physiology and biochemistry of vanadium has grown enormously in recent years.[2] Orthovanadate(V), an orthophosphate analogue, is a potent inhibitor of many phosphate metabolizing enzymes and has been used extensively to probe enzyme mechanisms.[2a-d] EPR studies with erythrocytes,[3] fat cells,[4] and yeast[5] have shown that vanadate(V) is rapidly acquired by cells and reduced intracellularly to the vanadyl(IV) ion, $VO^{2+}$, complexed with glutathione or proteins. However, dimeric vanadate(V) and decavanadate(V) as well as vanadyl(IV) have also been shown to accumulate within cells when yeast cultures are exposed to toxic levels of vanadate(V).[5] In the vanadium-rich blood cells of the tunicates *Ascidia ceratodes* and *A. nigra*[6] the $V^{3+}$ ion, possibly complexed to sulfate or tunichrome, is the principal species present. Small amounts of vanadyl(IV) ion are often found as well. Thus, under physiological conditions the +3, +4, and +5 oxidation states of the metal are accessible both kinetically and thermodynamically. The facility with which vanadium changes oxidation state may be a key to its biological function.

The physiological effects of vanadium on mammals are currently being studied in many laboratories.[2e,f] Early feeding studies suggest that trace amounts of vanadium are essential for normal growth and development of rats and chicks.[7] More recent work suggests that dietary vanadium may have cancer-preventative properties.[8] Although the iron-transport protein transferrin appears to transport dietary vanadium also,[9,10] the species of vanadium present in the circulation have not been completely identified. Vanadium administered intravenously to rats or dogs separates with the transferrin component of plasma during chromatography and electrophoresis.[9a] Similar results are obtained when the metal as vanadate(V) or vanadyl(IV) is administered to rats by gastric intubation.[10] Since recoveries are often in-

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