Solvation of Neodymium(III) Perchlorate and Nitrate in Organic Solvents as Determined by Spectroscopic Measurements*

JEAN-CLAUDE G. BÜNZLI** and MILAN M. VUCKOVIC

Université de Lausanne, Institut de Chimie Minérale et Analytique, Place du Château 3, CH-1005 Lausanne, Switzerland

Received October 27, 1983

The electronic absorption, emission spectra and fluorescence lifetimes of anhydrous and diluted (0.01–0.13 M) solutions of $Nd(ClO_4)_3$ and $Nd(NO_3)_3$ in CH_3CN, $(CH_3)_2CO$, DMSO, and DMF are used to investigate the solvation of the Nd(III) ion. Both the oscillator strengths and the lifetimes depend strongly upon the solvent; these latter range from 300 ns in $(CH_3)_2CO$ to 485 ns in DMF, 660 ns in CH_3CN, 1850 ns in DMSO, and 2300 ns in CD_3CN. Upon addition of nitrate to anhydrous solutions of $Nd(ClO_4)_3$ in poorly coordinating solvents, stable, inner-sphere complexes of formula $[Nd(NO_3)_n]^{(3-n)+}$ form, with n ≈ 1–5. The oscillator strength of the hypersensitive $^2G_{5/2}$, $^4G_{7/2} \leftarrow {}^4I_{9/2}$ transition increases strongly and linearly with the concentration of added nitrate. The addition of DMSO to anhydrous solution of $Nd(ClO_4)_3$ in CH_3CN results in the formation of an equilibrium between nona- and deca-coordinate species $[Nd(DMSO)_n]^{3+}$; the average number of coordinated DMSO molecules per Nd(III) ion is estimated to be 9.7 ± 0.8 from the lifetime data. In DMF, inner sphere nitrato complexes also form upon addition of nitrate to $Nd(ClO_4)_3$ solutions; equilibria take place that involve mono-, di-, and, possibly, tri-nitrato complexes, $[Nd(NO_3)_n]^{(3-n)+}$ with n = 1, 2, 3. The apparent equilibrium ratio for n = 1 is $K_1 = 110 \pm 30$ l·mol^{-1}.

The Ω_λ parameters, derived from the Judd-Ofelt theory, are calculated and discussed; in particular, Ω_λ is shown to increase linearly with the number of coordinated nitrate ions in the first coordination sphere. This number is estimated to be 1.5 for $Nd(NO_3)_3$ solutions 0.02 M in DMF. The relationship between Ω_λ and crystal field operators is discussed.

Introduction

The interest in the spectroscopic properties of neodymium(III) ions has been largely stimulated by its use in lasers, in the solid state, in glasses, and in

solutions [2]. Also, the discovery by Moeller and Ulrich that the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition in the yellow part of the visible spectrum is very sensitive to the environment of the metal ion [3] resulted in many studies which attempted to explain the hypersensitivity phenomenon [4], as well as in numerous applications taking advantage of this feature. For instance, the stability constant of [Nd(NO_3)]$^{2+}$ in water was determined [5] and a method for estimating the complexation constants was proposed [6].

Furthermore, a relationship between the shape of the hypersensitive absorption bands and the coordination number and symmetry of the lanthanide ion was discussed [7]. Finally, the electronic spectra of Nd(III) solutions in mono- and di-substituted amides [8], along with conductometric and ultrasonic absorption measurements, were used to investigate the nature and symmetry of the solvates and complexes formed in these solvents. In this communication we present a spectroscopic investigation of neodymium perchlorate and nitrate in anhydrous acetonitrile, acetone, dimethylformamide (DMF), and dimethylsulfoxide (DMSO). Both the absorption spectra and the fluorescence lifetimes are used to assess the nature of the complexes formed in solution. The results are compared with those presented in previous parts of this series for europium(III) [1, 9–11] and terbium(III) solutions [12].

Experimental

Preparation of the Solutions

Anhydrous $Nd(ClO_4)_3$ and $Nd(NO_3)_3$ were prepared from the oxide (99.9%, Glucydur) as previously described for the europium [13, 14] and terbium [12] salts. The purity of the salts was controlled by complexometric analyses, by their IR spectra and by their fluorescence lifetimes. The solvents CH_3CN, CD_3CN, $(CH_3)_2CO$, DMF, and DMSO were carefully dried before use. $NaClO_4$ and $NaNO_3$ were dehydrated under vacuum (10^{-2} mmHg/80 °C). All the solutions were prepared under a strictly controlled atmosphere (N_2 with less than 10 ppm water); their Nd-content was determined by complexometric analyses after completion of the measurements.

Spectroscopic Measurements

Absorption spectra were measured on a Hitachi-Perkin-Elmer 340 spectrometer equipped with a microprocessor; the ϵ vs. $\bar{\nu}$ data were transferred to a Hewlett-Packard 9825 A calculator to evaluate the band maxima and barycentres. The oscillator strengths were calculated according to

$$P = \frac{2303\, mc^2}{N\pi e^2} \cdot \frac{9n}{(n^2 + 2)^2} \cdot \int \epsilon(\bar{\nu})d\bar{\nu}$$

The refractive indices of the solutions, n, were measured at $20.0 \pm 0.1\ °C$ under daylight illumination with a Zeiss refractometer.
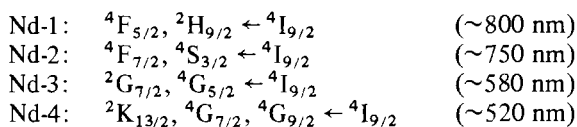
The emission lifetimes were calculated over at least 3 lifetimes after 512 accumulations: $\tau = 1/S$, S being the slope of $\ln I = f(t)$. The samples were excited by a pulsed neodymium laser with frequency doubler (530 nm, pulse width: 15 ns, pulse energy: 20 mJ). The emitted light (885 nm, $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition) was analyzed by a Bausch and Lomb grating monochromator and measured with a SHS-100 photodiode from EG and G. The signal was fed to a Tektronix R-7912 transient recorder coupled to a PDP 11/04 computer.

Results and Discussion

Solvent Effects on the Oscillator Strengths and Lifetimes of Dilute $Nd(ClO_4)_3$ Solutions

The four more intense absorption bands in the visible part of the Nd(III) spectrum were measured

as a function of the solvent for 0.01 M solutions of neodymium perchlorate (Table I); these transitions are labelled as follows:

Nd-1:	$^4F_{5/2}, {}^2H_{9/2} \leftarrow {}^4I_{9/2}$	($\sim$800 nm)
Nd-2:	$^4F_{7/2}, {}^4S_{3/2} \leftarrow {}^4I_{9/2}$	($\sim$750 nm)
Nd-3:	$^2G_{7/2}, {}^4G_{5/2} \leftarrow {}^4I_{9/2}$	($\sim$580 nm)
Nd-4:	$^2K_{13/2}, {}^4G_{7/2}, {}^4G_{9/2} \leftarrow {}^4I_{9/2}$	($\sim$520 nm)

The assignments are made by comparison with Carnall's data on aqueous solutions [15]. With respect to water, the transitions undergo a batho-chromic shift and their intensity increases for all the three solvents. The largest changes occur for the hypersensitive transition Nd-3 which is shifted by 210, 150, and 90 cm^{-1}; its oscillator strength increases by 40%, 80%, and 110% for solutions in DMSO, CH$_3$CN, and DMF respectively. This transition appears as a structured band, similar in shape to that observed for aqueous solutions; therefore, according to Karraker's criterion [7] the coordination number of the Nd(III) ion should be the same, nine [16]. Such comparisons are, however, essentially qualitative, so that we have studied the Nd(III) solvation in more detail (cf. following Sections).

The lifetimes reported in Table II were measured on 0.1 M solutions: in all cases, a single exponential decay was observed. Moreover, the lifetimes do not depend upon the excitation power (10–90 mJ) contrary to what was observed for solutions in PO-Cl$_3$/SnCl$_4$ [17]. The fluorescence quenching occurs

TABLE I. Wavenumbers ($\bar{\nu}_{max}$, cm^{-1}) and Oscillator Strengths P of Selected Nd(III) Transitions for Perchlorate Solutions 0.01 M in Various Solvents, at Room Temperature.

Transition[a]	H$_2$O[b]		DMSO			CH$_3$CN			DMF		
	$\bar{\nu}_{max}$	$10^6 \cdot$P	$\bar{\nu}_{max}$	$10^6 \cdot$P	P/P$_{aq}$	$\bar{\nu}_{max}$	$10^6 \cdot$P	P/P$_{aq}$	$\bar{\nu}_{max}$	$10^6 \cdot$P	P/P$_{aq}$
Nd-1	12 595	6.9	12 485	8.7	1.3	12 560	11.4	1.6	12 485	11.2	1.6
Nd-2	13 515	6.5	13 350	7.6	1.2	13 475	12.0	1.8	13 350	10.9	1.7
Nd-3	17 390	8.1	17 180	11.6	1.4	17 300	14.3	1.8	17 240	16.7	2.1
Nd-4	19 155	5.8	19 120	6.3	1.1	19 120	9.4	1.6	10 045	8.9	1.5

[a]See the text for the assignment of the transitions. [b]These data were recorded to calibrate our measurement method; they are within ±2% of those reported by Karraker [7].

TABLE II. Lifetimes of the $^4F_{3/2}$ Level of Nd(III) in Perchlorate Solutions 0.1 M in Various Solvents, along with Relevant Data. Observed Transition: $^4F_{3/2} \rightarrow {}^4I_{9/2}$.

	(CH$_3$)$_2$CO	CH$_3$CN	CD$_3$CN	DMF	DMSO
τ (ns)	300 ± 40	660 ± 30	2300 ± 110	485 ± 30	1850 ± 60
$\bar{\nu}_{A—B}$ (cm^{-1})[a]	1710	2254	2258	1680	1050
$\Delta E/\bar{\nu}_{A—B}$[b]	3.1	2.3	2.3	3.1	5.0
$\Delta E/\bar{\nu}_{C—H(D)}$[c]	1.8	1.8	2.3	1.8	1.8

[a]Stretch wavenumber, A = C, S. and B = O, N. [b]$\Delta E = E(^4F_{3/2}) - E(^4I_{15/2}) = 5280$ cm^{-1}. [c]$\bar{\nu}_{C—H} = 3000$ cm^{-1}, $\bar{\nu}_{C—D} = 2258$ cm^{-1}.
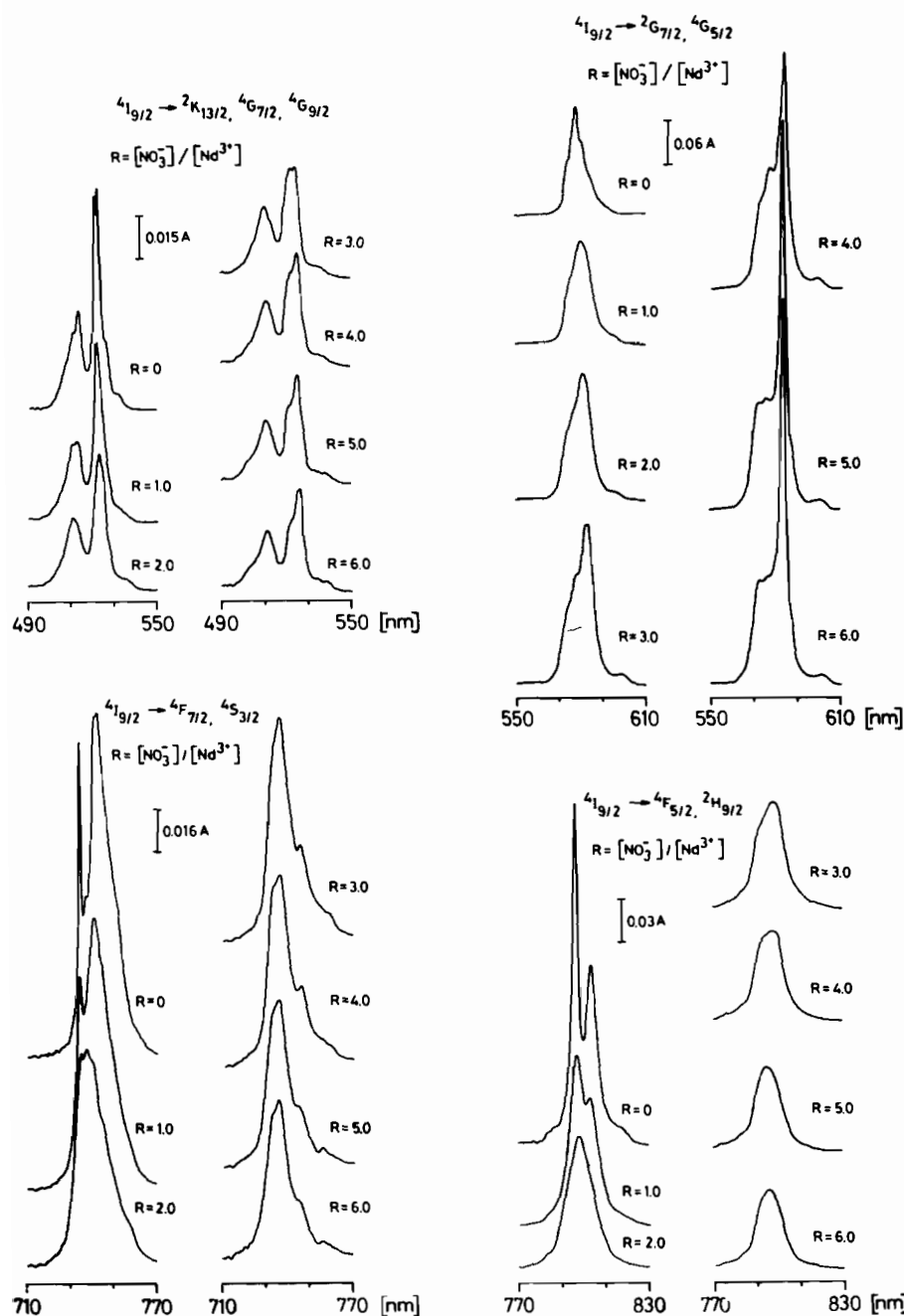
Fig. 1. Influence of the nitrate concentration on the absorption spectra of anhydrous $Nd(ClO_4)_3$ solutions $0.01\ M$ in acetonitrile.

via a multiphononic process; if we consider the vibrational stretching modes more likely to be involved, namely the C—H(D) one and the one involving the donor atom, we can calculate the number of phonons necessary to induce the $^4F_{3/2} \rightarrow {}^4I_{15/2}$ nonradiative transition: it ranges between 2 and 3, except for DMSO (*cf.* Table II). The influence of the C—H vibrations is evidenced by the increase in the lifetime from 660 to 2300 ns in going from CH_3CN to CD_3-CN. It may also explain the larger quenching effect of acetone as compared to acetonitrile, the former

containing two methyl groups instead of one for CH_3CN.

Complex Formation with Nitrate and with DMSO

When nitrate is added to anhydrous solutions of neodymium perchlorate in weakly coordinating solvents, both the shape of the absorption bands (Fig. 1), the oscillator strengths (Fig. 2, Table III), and the fluorescence lifetimes* (Table IV, Fig. 2)

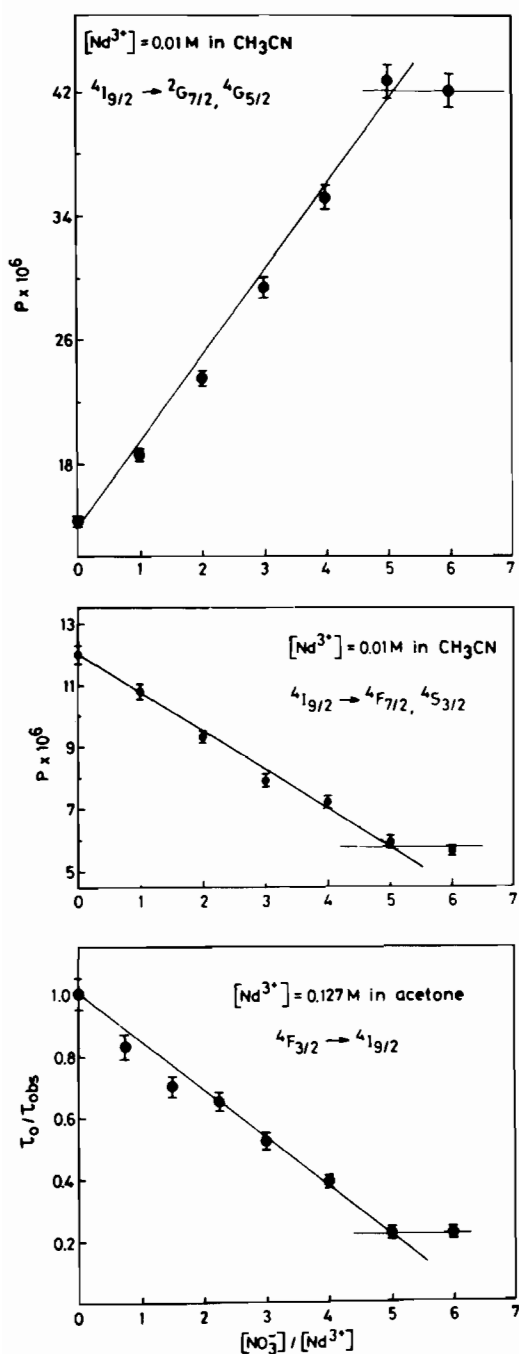*Acetone was used instead of acetonitrile, for solubility reasons.

Fig. 2. Influence of the nitrate concentration on the oscillator strengths of the $^2G_{7/2}$, $^4G_{5/2} \leftarrow ^4I_{9/2}$ (top) and $^4F_{7/2}$, $^5S_{3/2} \leftarrow ^4I_{9/2}$ (middle) transitions and on the lifetimes (bottom) of anhydrous solutions of $Nd(ClO_4)_3$ 0.010 M in CH_3-CN or 0.127 M in $(CH_3)_2CO$ (lifetimes).

TABLE III. Oscillator Strengths ($\times 10^6$) vs. the Concentration of Added Nitrate for Anhydrous Solutions of $Nd(ClO_4)_3$ 0.01 M in CH_3CN; $R = [NO_3^-]_t/[Nd^{3+}]_t$.

Transition[a]	R = 1	R = 2	R = 3	R = 4	R = 5	R = 6
Nd-1	8.8	8.0	6.6	5.6	4.9	4.7
Nd-2	10.8	9.3	7.9	7.2	5.9	5.6
Nd-3	18.6	23.5	19.4	35.2	42.7	42.2
Nd-4	8.5	7.7	7.4	7.3	7.3	6.8

[a]See the text for the assignment of the transitions.

TABLE IV. Lifetimes of Anhydrous $Nd(ClO_4)_3$ Solutions in Acetone, Acetonitrile or DMF vs. $R = [L]_t/[Nd^{3+}]_t$; $\lambda_{exc} = 530$ nm, $\lambda_{anal} = 885$ nm.

R	τ(ns)	R	τ(ns)
$L = NO_3^-$, $[Nd^{3+}] = 0.127 M$ in acetone			
0.7	350 ± 30	4.0	740 ± 40
1.5	415 ± 35	5.0	1320 ± 70
2.2	450 ± 40	6.0	1340 ± 60
3.0	560 ± 50		
$L = DMSO$, $[Nd^{3+}] = 0.128 M$, in acetonitrile			
2.0	800 ± 30	10.0	1850 ± 60
4.0	830 ± 40	12.0	1880 ± 60
6.0	1090 ± 40	14.0	1820 ± 50
8.0	1410 ± 50	18.8	1850 ± 60
$L = NO_3^-$, $[Nd^{3+}] = 0.1 M$ in DMF			
1.0	500 ± 50	5.0	585 ± 40
1.9	525 ± 50	6.0	585 ± 40
3.0	550 ± 50	7.0	575 ± 40
3.7	565 ± 50	8.0	575 ± 40
4.5	575 ± 40		

undergo large changes which reflect the formation of $[Nd(NO_3)_5]^{2-}$. A similar situation occurred for Ln = Eu [1] and Tb [12], while Walker and Weeden reported that in solution in methylene chloride and nitrobenzene, the hexanitrato complexes completely

dissociate into pentanitrates [18]. According to [4], the intensity of the hypersensitive transitions may be related to the electron-donor ability (basicity) of the ligands whereas the intensity of the non-hypersensitive transitions depends upon the symmetry of the complex. Our results are in agreement with the first part of this statement: the Nd-4 oscillator strength increases strongly and linearly with the nitrate concentration. The intensity of the other transitions decreases with increasing $[NO_3^-]$, Nd-1 and Nd-2 by a factor of 1.9, Nd-3 by a factor of 1.2. Another interesting point is the concordance between absorption and lifetime data. Since the former reflect complex formation in the ground state whereas the latter give information on the Nd(III) excited state, one can conclude that no substantial change occurs in the inner coordination sphere upon excitation, contrary to what is observed for Gd(III) in aqueous solutions [19]. The Stern-Völmer quenching constant [12] calculated from the lifetime data is 1.16 ± 0.04

$1 \cdot mol^{-1}$. The slight deviation from linearity of the Stern-Völmer plot in Fig. 2 for small values of $R = [NO_3^-]_t/[Nd^{3+}]_t$ probably arises from the presence of perchlorate in the inner coordination sphere of Nd(III) [20].

Similar measurements were performed on anhydrous $Nd(ClO_4)_3$ solutions containing various amounts of DMSO. The oscillator strength of the hypersensitive Nd-3 transition first increases slightly up to $R = [DMSO]_t/[Nd^{3+}]_t = 4$ and then decreases sharply up to $R \sim 10$ (Fig. 3). The intensities of the
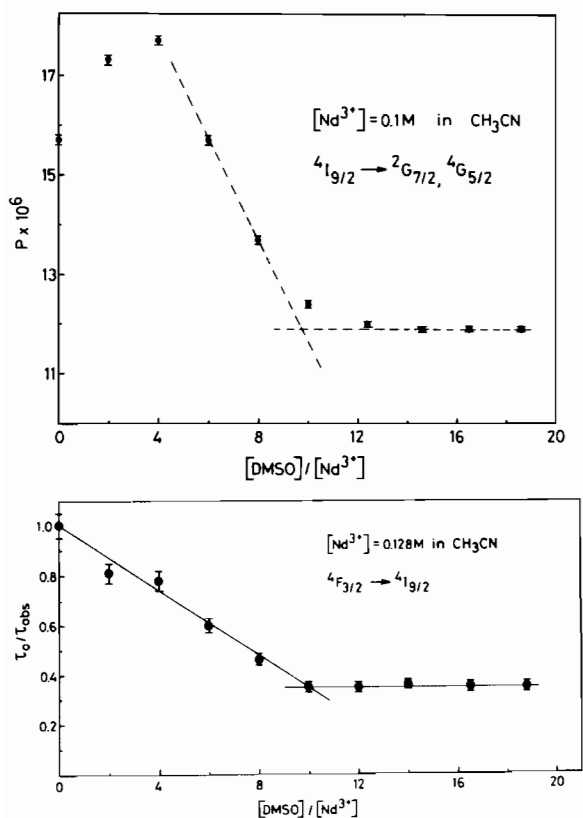

Fig. 3. Influence of the DMSO concentration on the oscillator strength of the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition (top) and of the lifetimes (bottom) of anhydrous solutions of $Nd(ClO_4)_3$ 0.128 M in CH_3CN.

other transitions decrease by 30–35% between $R = 0$ and $R = 4$ and then remain approximately constant. The data for $R \leqslant 4$ reflect the replacement of the inner-sphere coordinated perchlorate [20] by DMSO molecules, as confirmed by conductivity measurements on 0.01 M solutions: the molar conductance increases from 208 to 242 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ between $R = 0$ and $R = 4.5$, and then remains constant; these values are characteristic for a 2:1 electrolyte [11]. We have however no explanation for the absolute variation of P(Nd-3) *vs.* R and for the constancy of the other transition intensities for $R > 4$, despite the changes that still occur in the inner coordination

sphere. The fluorescence lifetimes (Table IV, Fig. 3) increase upon addition of DMSO. The resulting Stern-Völmer plot is strictly linear for $R > 4$ and horizontal for $R > 10$, the intersection being at $R = 9.7 \pm 0.8$; the corresponding quenching constant amounts to 0.50 ± 0.03 $1 \cdot mol^{-1}$, approximately half the value observed for nitrate. From both the P(Nd-3) and the lifetime data we conclude the formation of an equilibrium between $[Nd(DMSO)_n]^{3+}$ species with $n = 9$ and 10 when $R > 10$. Lugina *et al.* have deduced from electronic and IR absorption data the presence of similar equilibria between species with $n = 8$ and 9 in DMSO/water [21] and $CH_3NO_2/DMSO$ [22] mixtures. Detailed FT IR measurements point to an average coordination number slightly larger than 9 [20] for Nd(III) in $CH_3CN/DMSO$ mixtures in agreement with our (rather inaccurate) estimate.

Solvation of Neodymium Perchlorate and Nitrate in DMF

Neodymium perchlorate is a 3:1 electrolyte in DMF [8] and absorption spectra are consistent with a first coordination sphere essentially comprised of solvent molecules [23]. In fact, a recent temperature- and pressure-dependent study [24] has shown the presence of an equilibrium between an octa- and a nona-coordinate species $[Nd(DMF)_n]^{3+}$. Nevertheless, we have found a slight dependence of the fluorescence lifetime of anhydrous $Nd(ClO_4)_3$ solutions 0.1 M in DMF with the perchlorate concentration: τ increases from 485 ± 30 to 505 ± 30 and 535 ± 30 ns when $[ClO_4^-]_t/[Nd^{3+}]_t$ is increased from 3 to 6 and 9 respectively. This effect reflects a weak, possibly outer-sphere, ClO_4^-/Nd^{3+} interaction.

When nitrate is added to $Nd(ClO_4)_3$ solutions in DMF, both the absorption band shapes (Fig. 4), the oscillator strengths (Table V), and the lifetimes (Table IV) undergo substantial changes reflecting the formation of inner sphere nitrato complexes; this conclusion is in agreement with spectroscopic data, ultrasonic absorption spectra and conductivities of $Nd(NO_3)_3$ in DMF [8], but contradicts an earlier report [25]. The intensity changes, as well as the Stern-Völmer plot (Fig. 5), point to the presence of equilibria between different species $[Nd(NO_3)_n-(DMF)_x]^{(3-n)+}$, with $n = 1$, 2 and possibly 3, as was observed for Eu(III) [9]. Conductometric data for $Nd(NO_3)_3$ solutions [8] indeed show a gradual shift from a 2:1 (<0.002 M) to a 1:1 electrolyte (<0.1 M) and even to a non-electrolyte (0.2 M) behaviour. Using known procedures [26], we have estimated the apparent equilibrium ratios K_n form the P(Nd-3) data:

$$K_n = \frac{[Nd(NO_3)_n(DMF)_x]^{(3-n)+}}{[Nd(NO_3)_{n-1}(DMF)_y]^{(4-n)+}[NO_3^-]}$$

TABLE V. Oscillator strengths ($\times 10^6$) vs. the Concentration of Added Nitrate for Anhydrous Solutions of Nd(ClO$_4$)$_3$ 0.018 M in DMF; R = [NO$_3^-$]$_t$/Nd^{3+}]$_t$.

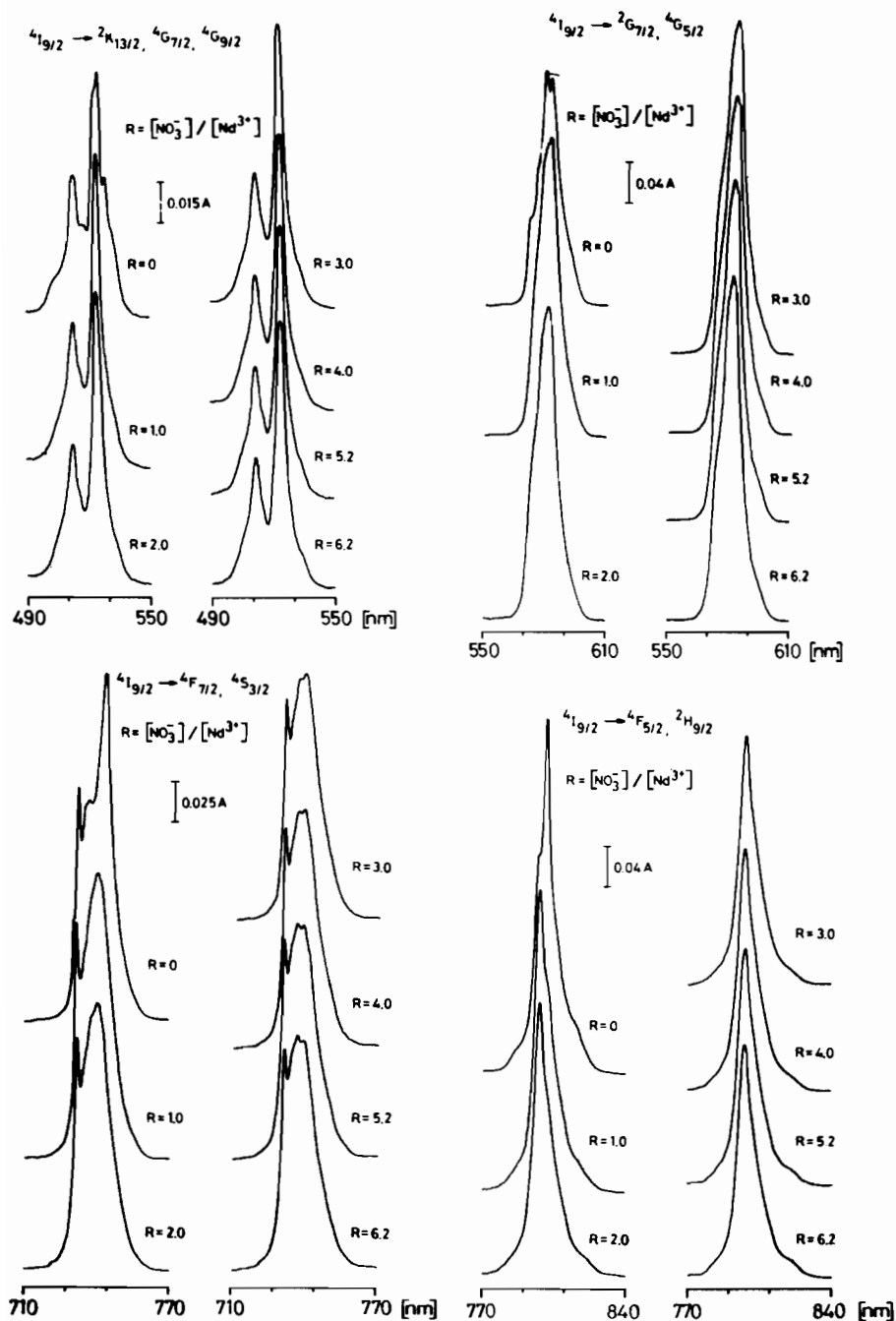| Transition[a]	R = 1.0	R = 2.0	R = 3.0	R = 4.0	R = 5.2	R = 6.2
Nd-1	10.5	9.5	9.0	8.9	8.8	8.7
Nd-2	10.6	10.0	9.7	9.5	9.2	9.1
Nd-3	21.7	23.1	23.7	24.1	24.2	24.4
Nd-4	9.1	8.8	8.5	8.4	8.4	8.3

[a]See the text for the assignment of the transitions.

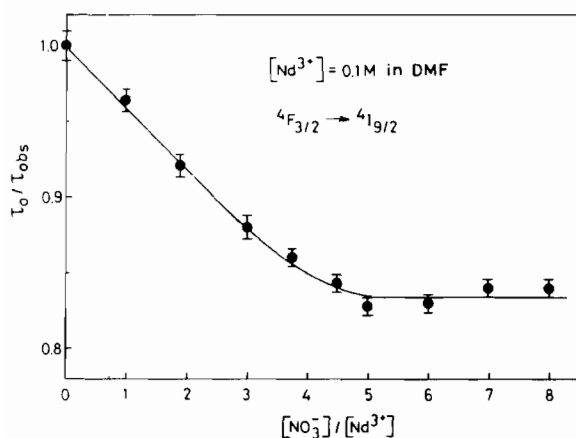Fig. 4. Influence of the nitrate concentration on the absorption spectra of anhydrous Nd(ClO$_4$)$_3$ solutions 0.018 M in DMF.

Fig. 5. Stern-Völmer plot for anhydrous $Nd(ClO_4)_3$ solutions 0.1 M in DMF containing various amounts of nitrate.

We find $K_1 = 110 \pm 30$ $l \cdot mol^{-1}$ and $K_2 \approx 260$ $l \cdot mol^{-1}$. These values are to be taken as indicative only.

Complexation Effects on the Ω_λ Parameters

In order to summarize the influence of the ligands on the oscillator strengths of the f–f transitions we have evaluated, by a least-squares procedure, the Ω_λ parameters [15], which are deduced from the Judd-Ofelt T_λ parameters:

$$P = \sum_{2,4,6} \bar{\nu} T_\lambda \langle f^3 \psi_J \| U^{(\lambda)} \| f^3 \psi'_{J'} \rangle^2$$

$$\Omega_\lambda = (2J + 1)T_\lambda \cdot \frac{3h}{8\pi^2 mc} \cdot \frac{9n}{(n^2 + 2)^2}$$

The results are presented in Table VI, along with comparative data. These parameters are difficult to link to a unique property of the ligands. However, Reisfeld and Jørgensen [2] have shown Ω_2 to be quite sensitive to the metal-ion surroundings, so that this parameter is often associated with hypersensitivity. In particular, its value increases considerably

TABLE VI. Ω_λ Parameters ($\times 10^{20}$, cm^2) for Various Nd(III) Solutions with $[Nd^{3+}]$ Between 0.01 and 0.02 M.

Salt	Solvent	Ω_2	Ω_4	Ω_6
$Nd(ClO_4)_3$	H_2O [2]	0.93	5.0	7.9
	CH_3CN	1.2	7.7	9.8
	DMF	1.2	8.9	8.4
$Nd(NO_3)_3$	CH_3CN	11.8	2.1	6.6
	DMF	6.7	5.0	7.6
	TBP[a] [27]	11.5	3.2	8.9
$(Me_4N)_2Nd(NO_3)_5$	CH_3CN	18.7	1.0	4.9
$Nd(acac)_3$[a]	DMF[b] [2]	24.5	0.71	9.1

[a]Tributylphosphate.   [b]Acetylacetonate.

when anionic ligands, either conjugated (acetylacetonate) or polarizable (nitrate), are bonded in the inner coordination sphere. This is reflected by our data: perchlorate solutions in CH_3CN and DMF have the same Ω_2 whereas this parameter increases considerably, *and linearly*, with the number of nitrate ions in the first coordination sphere of the Nd(III) ion in acetonitrile solutions.

Taking advantage of this linear correlation, we calculate an average number of inner-sphere coordinated nitrate ions per neodymium ion, ñ, equal to 1.5 in 0.02 M solutions of $Nd(NO_3)_3$ in DMF. This value is in agreement with the conductometric data [8] and with ñ = 1.8 found for $Eu(NO_3)_3$ solutions 0.05 in DMF [9]. For these latter solutions, the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition also increases linearly with ñ.

If the Racah formalism is used to calculate the f–f transition intensities [28], taking into account the J-mixing [29], one finds that the Ω_λ parameters essentially depend upon the following C_q^k operators*:

$\lambda = 2$ $k = 1, 3$
$\lambda = 4$ $k = 3, 5$
$\lambda = 6$ $k = 5, 7$

When nitrate is added to $Nd(ClO_4)_3$ solutions, Ω_4 and Ω_6 decrease, but Ω_2 increases considerably, which is therefore due solely to the matrix element containing C_q^{1}.

Acknowledgement

References

1 J.-C. G. Bünzli and J.-R. Yersin, *Inorg. Chim. Acta, 94*, 301 (1984).
2 R. Reisfeld and C. K. Jørgensen, 'Lasers and Excited State of Rare Earths', Springer Verlag, Berlin, 1977.
3 T. Möller and W. F. Ulrich, *J. Inorg. Nucl. Chem., 2*, 164 (1956).
4 D. E. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev., 18*, 199 (1976).
5 N. A. Coward and R. W. Kiser, *J. Phys. Chem., 70*, 213 (1966); V. M. Barinov, L. G. Tebelev, A. G. Rykov and

*The Nd-2 and Nd-3 transitions only are considered here.

G. N. Yakoulev, *Russ. J. Inorg. Chem. (Engl. transl.)*, *14*, 207 (1969).

6 K. Bukietynska, A. Mondry and E. Osmeda, *J. Inorg. Nucl. Chem.*, *39*, 483 (1977); *ibid.*, *J. Inorg. Nucl. Chem.*, *43*, 1311 and 1321 (1981).

7 D. G. Karraker, *Inorg. Chem.*, *6*, 1863 (1967); *ibid.*, *Inorg. Chem.*, *7*, 473 (1968).

8 J. Legendziewicz, K. Bukietynska and G. Oczko, *J. Inorg. Nucl. Chem.*, *43*, 1293 (1981).

9 J.-C. G. Bünzli and J.-R. Yersin, *Helv. Chim. Acta*, *65*, 2498 (1982).

10 J.-C. G. Bünzli, C. Mabillard and J.-R. Yersin, *Inorg. Chem.*, *21*, 4214 (1982).

11 J.-C. G. Bünzli, J.-R. Yersin and C. Mabillard, *Inorg. Chem.*, *21*, 1471 (1982).

12 J.-C. G. Bünzli and M. Vuckovic, *Inorg. Chim. Acta*, *73*, 53 (1983).

13 J.-C. G. Bünzli, E. Moret and J.-R. Yersin, *Helv. Chim. Acta*, *61*, 762 (1978).

14 J.-C. G. Bünzli and J.-R. Yersin, *Inorg. Chem.*, *18*, 605 (1979).

15 W. T. Carnall in 'Handbook on the Physics and Chemistry of Rare Earths', K. A. Gschneidner, Jr., Le Roy Eyring, Eds., North Holland Publishing Co., Amsterdam, 1979; Vol. 3, Ch. 24.

16 A. Habenschuss and F. H. Spedding, *J. Chem. Phys.*, *70*, 2797 (1979).

17 A. V. Aristov, V. P. Kolobkov, P. I. Kudryashov and V.

S. Shevaudin, *Opt. Spectrosc. (Engl. transl.)*, *39*, 160 (1975).

18 I. M. Walker and D. H. Weeden, *Inorg. Chem.*, *12*, 772 (1973).

19 M. D. Marcantonatos, M. Deschaux and J. J. Vuilleumier, *Chem. Phys. Letters*, *91*, 149 (1982).

20 C. Mabillard, Ph.D. Thesis, Nr. 505, Ecole Polytechnique Fédérale, Lausanne, 1983.

21 L. N. Lugina, N. K. Davidenko and K. B. Yatsimirskii, *Russ. J. Inorg. Chem. (Engl. transl.)*, *18*, 1453 (1973).

22 L. N. Lugina and N. K. Davidenko, *Russ. J. Inorg. Chem. (Engl. transl.)*, *25*, 1322 (1980).

23 J. Legendziewicz, K. Bukietynska, Z. Kopaczynska and B. Jezowska-Trzebiatowska, *Opt. Spectrosc. (Engl. transl.)*, *45*, 160 (1978).

24 D. L. Pisaniello, P. J. Nichols, Y. Ducommun and A. E. Merbach, *Helv. Chim. Acta*, *65*, 1025 (1982).

25 I. Abrahamer and Y. Marcus, *J. Inorg. Nucl. Chem.*, *30*, 1563 (1968).

26 F. J. C. Rossotti, H. S. Rossotti and R. J. Whewell, *J. Inorg. Nucl. Chem.*, *33*, 2051 (1971); P. Gans, *Coord. Chem. Rev.*, *19*, 99 (1976).

27 D. E. Henrie and C. E. Smyser, *J. Inorg. Nucl. Chem.*, *39*, 625 (1977).

28 P. Caro, 'Structure électronique des éléments de transition', Collection SUP, Presses Universitaires de France, Paris 1976.

29 P. Porcher and P. Caro, *J. Luminesc.*, *21*, 207 (1980).