FT-IR and fluorometric investigation of rare-earth and metal ion solvation
Part 11. Interaction between DMSO and lanthanide perchlorates in anhydrous acetonitrile*

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(Received August 5, 1991; revised October 18, 1991)

Abstract

The interaction between DMSO and lanthanide perchlorates in anhydrous acetonitrile has been investigated by FT-IR and Raman spectroscopy. A quantitative study was performed on 0.05 M solutions with $R=[\mathrm{DMSO}]_t/[\mathrm{Ln}]_t=7$–20. The ν_7(S–O) vibration of DMSO was used to determine the concentration of free DMSO in solution. None of the investigated systems shows any interaction with either perchlorate ions or acetonitrile molecules. The average coordination number (*CN*) of the Ln(III) ions is therefore equal to the average number of bonded DMSO molecules. Changes in coordination numbers are observed both with increasing atomic number and with the solvent composition. The data may be interpreted in terms of equilibria between six-, seven-, eight-, nine- and ten-coordinate species. For $R=8$, a gradual change is observed between 7.8 (La) and 6.6 (Lu). For $R=12$ and 15, the overall change amounts to 1.3 ($8.7-7.4$) and 1.7 units ($9.7-8.0$), respectively, but in addition, a clear discontinuity is observed at Gd (c. 1 unit). For $R=15$, additional breaks (c. 0.5 unit) occur around Nd and Er. For a single ion, changes in coordination number with increasing DMSO composition ($R=7$–15) amounts to almost 2 units for lighter Ln ions and to 1.0–1.2 units for heavier ions. All the DMSO molecules in the inner-coordination sphere appear to be equivalent, so that the increase in *CN* is interpreted in terms of an expansion of the first coordination sphere to accommodate additional donor molecules. Equilibrium constants have been estimated from the average *CN*s. They vary between log $K_8=2.2$ (La) to 0.6 (Lu), log $K_9=1$ (La) to 0.4 (Lu) and log $K_{10}=0.9$ (La) to 0.3 (Sm).

Introduction

Trivalent ions belonging to the lanthanide series (La–Lu) are characterized by the regular filling of internal 4f orbitals. Their complexes and solvates are dominated by strong ion–dipole interactions, and the number and arrangement of the ligands in the primary coordination sphere are the result of an interplay between electrostatic and steric factors. Several aspects of the coordination chemistry of lanthanide ions in solution remain unclear because of the presence of equilibria between differently coordinated species or between species with the same coordination number but with different geometries [1, 2]. It has been established that the hydration number of the aquo ions varies between 9 (or 10) for the lighter and 8 for the heavier lanthanides [3–5]. Coordination numbers of trivalent lanthanide ions as well as their interaction with anions in water, non-aqueous and mixed solutions are being systematically investigated in our laboratory by means of various experimental techniques such as UV–Vis absorption spectroscopy [6], luminescence [7–13], ^{139}La NMR [14] and Fourier transform infrared spectroscopy (FT-IR) [10, 11, 15–18]. The latter technique is very convenient for quantitative analyses leading to a precise determination of coordination numbers. We have recently reported a systematic study of lanthanide nitrate solutions in anhydrous acetonitrile containing DMSO [17]. Changes of the average coordination number (*CN*) along the Ln series and with the DMSO concentration are unambiguously demonstrated. For instance, for $R=[\mathrm{DMSO}]_t/[\mathrm{Ln}]_t$ ranging from 2 to 6, there are equilibria between ten- and nine-coordinate species for the lighter lanthanides and between nine- and eight-coordinate species for the intermediate and heavier ions. The average *CN* values increase with increasing DMSO concentration. We have also inves-

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*For Part 10 see ref. 18.

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0020-1693/92/$5.00

tigated the interaction between Ln(III) and perchlorate ions in anhydrous acetonitrile [18], bringing experimental evidences for the formation of moderately stable inner-sphere complexes with both mono- and bidentate perchlorate ions.

In this communication we present the systematic study of the interaction between DMSO and lanthanide perchlorates in anhydrous acetonitrile. Average coordination numbers for different compositions of the solution ($R=8, 12, 15$) are determined and the apparent stability constants for the fixation of the last DMSO molecules are extracted from these data.

Experimental

Synthesis of the complexes and preparation of the solutions

Hydrated lanthanide perchlorates were prepared from 99.9% or 99.99% (Research Chemicals or Apache Chemicals) pure oxides and reagent grade perchloric acid (Merck). Crystalline adducts $Ln(ClO_4)_3 \cdot n$DMSO were synthesized from hydrated lanthanide perchlorates according to ref. 19, then dried *in vacuo* over P_4O_{10}. The number n of DMSO molecules bonded to the lanthanide ion was calculated from the results of complexometric titrations using Titriplex III (Merck) in the presence of urotropine and xylene-orange: $n=8.0$ (La–Nd), 7.3 (Sm), 7.4 (Eu), 7.0 (Gd–Lu). Part of the DMSO is removed if the complex is kept in the desiccator for several days: n stabilizes around 6.7 for all the lanthanides.

Acetonitrile (Fluka, puriss) was treated with CaH_2 and P_4O_{10}, distilled three times and finally stored over 3 Å molecular sieves. The water content, checked by Karl Fischer titration using a Mettler DL-18 apparatus, was between 20 and 30 ppm. DMSO (Fluka, spectroscopic quality) was dried over 3 Å molecular sieves. Lanthanide solutions were prepared in a glove box under inert atmosphere (N_2 containing less than 10 ppm water). The lanthanide ion concentration of the solutions, usually 0.05 M, was determined by complexometric titration. Because of solubility problems, a lower concentration (0.025 M) was used for La-containing solutions.

Spectroscopic measurements

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 by the interference fringe method [20] and the observed absorbances were corrected accordingly. Raman spectra were measured with a Spex Ramalog-4 instrument using excitation at 514.5 nm of an Ar laser (Spectra Physics, Stabilite 2016). Liquid cells (IR measurements) and capillaries (Raman measurements) were filled in the glove box. Decomposition of IR and Raman spectra into individual components was performed on a VAX-8550 computer using Lorentzian functions to simulate the absorption and emission lines [21].

Results and discussion

FT-IR and Raman spectra

Several among the 24 vibrational modes of dimethyl sulfoxide are affected by the complexation with the lanthanide ions. They are listed in Table 1, along with their assignment in C_s symmetry [22]. The largest shifts occur for the S–O (ν_7) and C–S (ν_{22}) stretching vibrations. The ν_7 shift increases with increasing atomic number of the Ln(III) iron, from -49 to -58 cm^{-1}, and slightly decreases with increasing DMSO concentration. The bathochromic effect is characteristic of coordination through the oxygen atom. The other shifts are opposite in sign and smaller (11–22 cm^{-1}), but show the same tendencies as the ν_7 shift, although to a much lesser extent. These data are similar to those observed for lanthanide nitrate solutions [17]. For the latter, however, the increase of the shifts with Z was smaller and ν_6 $\delta(CH_3)$ displayed a slight bathochromic displacement upon complexation.

Typical FT-IR difference spectra of 0.05 M solutions of lanthanide perchlorates in anhydrous acetonitrile are partly reproduced in Fig. 1 for several values of $R=[DMSO]_t/[Ln]_t$. When solid adducts $[Ln(DMSO)_7](ClO_4)_3$ are dissolved in acetonitrile, absorption bands of both bonded and free DMSO appear in the spectra. However, the main vibration of free DMSO (ν_7, 1060 cm^{-1}) gives rise to a fairly small band, the intensity of which increases upon addition of increasing amounts of DMSO. The ν_7 (coordinated) $-$ ν_7 (free) shift reflects the magnitude of the Ln–DMSO interaction (Fig. 2). For a constant composition of the solution this shift increases with Z, reflecting the increase in electrostatic interaction through the series. The decrease of this shift with increasing DMSO concentration is interpreted as arising from a steric effect when more DMSO molecules are coordinated to the Ln(III) ion.

The ν_7 vibration of free DMSO is an asymmetric band comprised of two components, ν_7^a and ν_7^b [22]; it interferes with the low intensity ν_{20} $r(CH_3)$ vibration,

TABLE 1. Observed shifts, ν (coordinated) $-\nu$ (free) ($\pm 1\ \mathrm{cm^{-1}}$), for vibrations assigned to coordinated DMSO molecules in 0.05 M solutions of $\mathrm{Ln(ClO_4)_3 \cdot}n\mathrm{DMSO}$ in acetonitrile containing DMSO[a]

Ln	R[b]	ν_{22}[c] ν(CS)A″ 697[d]	ν_9 $r(\mathrm{CH_3})$A″ 927	ν_{21} $r(\mathrm{CH_3})$A′ 950	ν_{20} $r(\mathrm{CH_3})$A′ 1016	ν_7 ν(SO)A′ 1060	ν_6 $\delta(\mathrm{CH_3})$A′ 1309
La[e]	8	18	13	11	9	−49	11
	12	18	13	10	8	−48	11
	15	18	14	10	16	−48	11
Ce	8	18	14	11	11	−51	11
	12	18	13	10	9	−50	11
	15	18	14	10	–	−50	11
Pr	8	19	14	11	14	−51	11
	12	18	14	11	14	−50	11
	15	18	14	10	15	−49	11
Nd	8	19	14	12	13	−53	12
	12	18	13	11	13	−51	11
	15	18	14	11	14	−50	9
Sm	8	19	14	12	12	−52	12
	12	19	14	12	13	−51	11
	15	19	14	11	15	−51	11
Eu	8	19	15	12	12	−54	11
	12	19	14	12	12	−52	11
	15	19	14	12	13	−51	11
Gd	8	19	15	12	12	−53	12
	12	19	15	12	13	−51	11
	15	19	14	12	13	−51	11
Tb	8	19	15	13	12	−53	11
	12	19	14	12	12	−51	11
	15	19	15	12	13	−51	11
Dy	8	20	15	13	13	−54	11
	12	19	15	13	12	−52	11
	15	19	15	13	12	−51	12
Ho	8	20	15	13	13	−57	13
	12	20	15	13	12	−52	12
	15	19	14	13	12	−51	11
Er	8	21	16	13	13	−56	13
	12	20	16	13	9	−56	13
	15	19	15	13	14	−51	12
Tm	8	21	16	14	13	−59	14
	12	21	15	13	12	−55	13
	15	20	15	13	13	−55	12
Yb	8	21	15	14	11	−59	13
	12	21	15	13	13	−59	13
	15	20	15	13	12	−59	13
Lu	8	22	16	14	12	−58	14
	12	21	15	14	13	−58	14
	15	21	15	14	13	−58	14

[a] IR data for ν_7(SO) and ν_{20} r($\mathrm{CH_3}$) vibrations of bonded DMSO obtained from curve-resolved spectra are available from the authors upon request. [b] $R = [\mathrm{DMSO}]_t/[\mathrm{Ln}]_t$. [c] The assignments are made on the basis of a C_s symmetry [22]. [d] Vibrational frequencies of free DMSO in a 0.6 M solution in acetonitrile. [e] 0.025 M.

so that a curve fitting procedure had to be used to perform a quantitative analysis. Indeed, the concentration of free DMSO has been determined with the help of a calibration curve, in order to calculate the number *n* of DMSO molecules actually bonded to the Ln(III) ions. The experimental spectrum of free DMSO

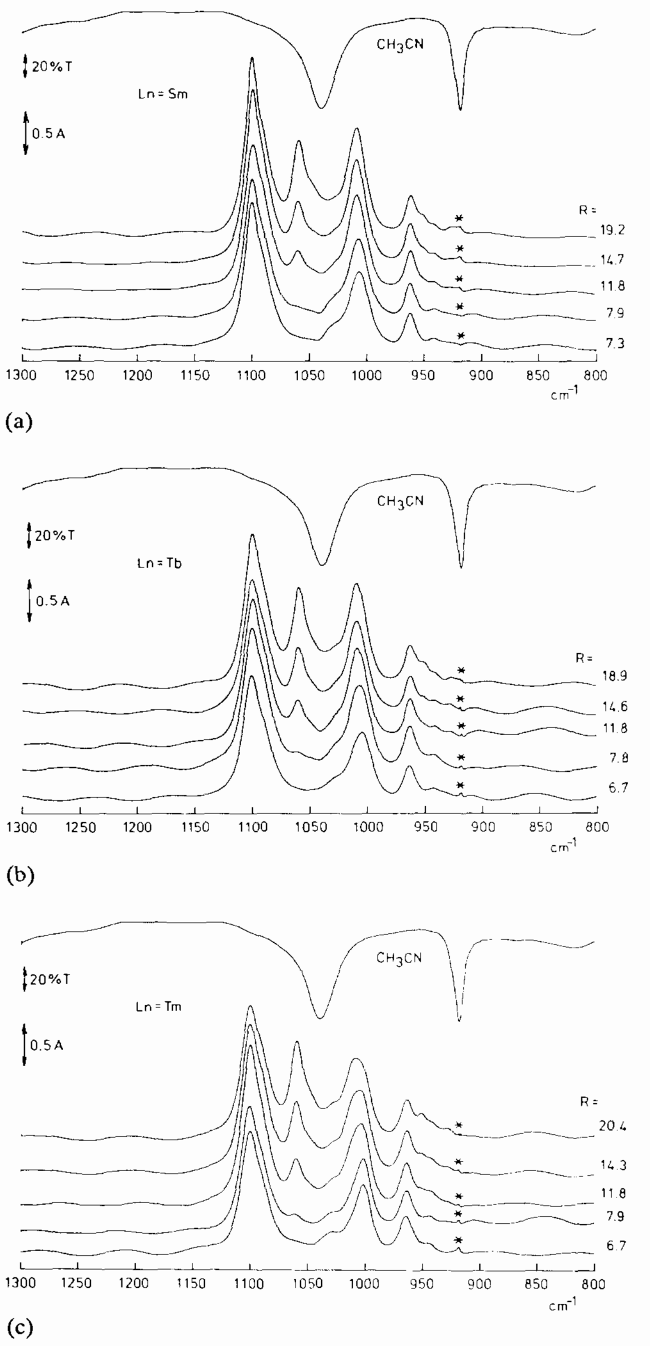

Fig. 1. Part of the FT-IR difference spectra of $Ln(ClO_4)_3 \cdot n$DMSO solutions 0.05 M in acetonitrile containing DMSO ($R = [DMSO]_t/[Ln]_t$). The upper trace represents the spectrum of CH_3CN in transmission units. Stars denote incomplete compensation of the solvent.

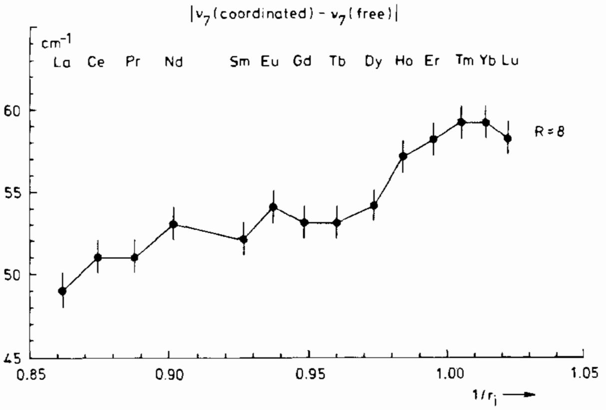

Fig. 2. Shift of the ν_7 vibration of DMSO upon coordination to Ln(III) in solutions of $Ln(ClO_4)_3 \cdot n$DMSO 0.05 M in acetonitrile with $R = [DMSO]_t/[Ln]_t = 8$.

has been simulated by three Lorentzian curves* in the range 1150–980 cm^{-1}: $\nu_7{}^a$ at 1060 cm^{-1}, full width at half height, fwhh = 11 cm^{-1}; $\nu_7{}^b$ at 1049 cm^{-1}, fwhh = 21 cm^{-1}; ν_{20} at 1016 cm^{-1}, fwhh = 13 cm^{-1}. For $Ln(ClO_4)_3 \cdot n$DMSO solutions, FT-IR difference spectra become more complex with the presence of the asymmetric $\nu_3(T_2)$ perchlorate vibration (two components [10]) and the $\nu_7{}^a$, $\nu_7{}^b$, and ν_{20} vibrations of bonded DMSO molecules. The results of typical spectral decompositions for two Ln solutions and two values of R are given in Fig. 3. In order to minimize the inaccuracy of the procedure, the linewidth of each component, as well as the position of the bands of free DMSO, were kept constant during the calculation.

Lugina and Davidenko have studied the complexation of Pr, Nd, Er and Lu perchlorates with DMSO in nitromethane [23]. In the case of lutetium, they report three bands in the 1000–1030 cm^{-1} spectral range and assign them to bonded DMSO molecules. In addition, they suggest that the band of lowest wavenumber at 1000 cm^{-1} ($\nu_7{}^a$ in our study) arises from DMSO molecules in the inner-coordination sphere while the other two bands at 1010 and 1029 cm^{-1} are representative of molecules coordinated in the outer-coordination sphere. We cannot accept this interpretation for the following reasons. (i) The ν_{20} vibration has been overlooked by the Russian authors as well as the fact that the ν_7 vibrational mode gives rise to an asymmetric band which has to be resolved into two components. The separation between these components is 10 cm^{-1} for both free and bonded DMSO molecules and is independent of the Ln(III) ion. (ii) For a given ratio R, the intensity of the weak band at *c.* 1029 cm^{-1} remains fairly constant along the lanthanide series, which should not be the case if equilibria involving the outer-coordination sphere were involved. (iii) If the band at *c.* 1029 cm^{-1} is assigned to the ν_{20} vibration of complexed DMSO molecules, the resulting shift (9–12 cm^{-1}) is close to those observed for the other CH_3

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*In a previous paper [10] a fourth, very weak, component was introduced at *c.* 1035 cm^{-1} in order to account for incomplete compensation of a solvent band, but this procedure proved to be unnecessary and even troublesome.

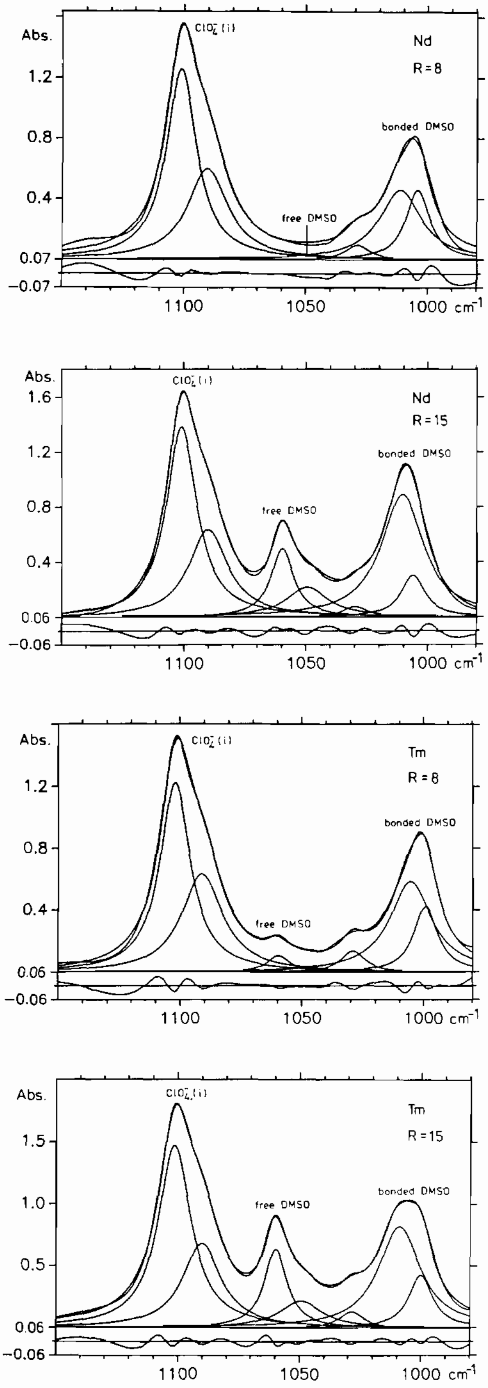

Fig. 3. Curve analysis of the FT-IR difference spectra of $Ln(ClO_4)_3 \cdot n$DMSO 0.05 M in acetonitrile with various amounts of DMSO ($R = [DMSO]_t/[Ln]_t$).

vibrations: 9–14, 13–16 and 11–13 cm^{-1} for ν_6, ν_9 and ν_{21}, respectively (cf. Table 1). (iv) Finally, the energy shifts between the free DMSO vibration $\nu_7{}^a$ at 1060 cm^{-1} and the other vibrations observed between 1010 and 1030 cm^{-1} are too large to assign the latter to DMSO molecules in the second coordination sphere.

The Raman spectra of several solutions were also investigated and the assignments of three of them are given in Table 2. For studying the interaction between DMSO and Ln(III) ions, we have selected the 650–720 cm^{-1} spectral range in which appear the intense ν_{10} vibration corresponding to the symmetric C–S stretch and the ν_{22} vibration corresponding to the asymmetric C–S stretch. The intensity of the ν_7 (S–O) vibration is indeed much smaller: Raman intensities depend on the polarizability of the chemical bond, which is higher for the C–S bond. The energy shift ν_{10} (coordinated) $-\nu_{10}$ (free) increases with increasing Z, 11 cm^{-1} for Pr and 16 cm^{-1} for Lu. The experimental spectrum of the Lu solution can be simulated by four Lorentzian curves: ν_{10} (free) at 667 cm^{-1}, fwhh = 10 cm^{-1}; ν_{10} (bonded) at 679 cm^{-1}, fwhh = 8 cm^{-1}; ν_{22} (free) at 699 cm^{-1}, fwhh = 13 cm^{-1}; ν_{22} (bonded) at 714 cm^{-1}, fwhh = 12 cm^{-1} (Fig. 4). Similar results are obtained for the other Ln(III) ions.

TABLE 2. Raman shifts observed for solutions of $Ln(ClO_4)_3 \cdot n$DMSO 0.05 M in acetonitrile with $R = [DMSO]_t/[Ln]_t = 20$

Wavenumber (cm^{-1})			Assignment	ν^a
Pr	Tb	Lu		
308	308	308	δ(CSC)A′DMSO[b]	ν_{12}
332	332	332	γ(SO)A″DMSO[b]	ν_{23}
379	379	379	δ(SO)A′DMSO[b]	ν_{11}
			$\delta(CCN)CH_3CN$	ν_8
458	458	458	$\delta_s(OClO)ClO_4^-$	ν_2
626	626	626	$\delta_{as}(OClO)ClO_4^-$	ν_4
666	666	666	ν_s(CSC)A′DMSO free	ν_{10}
677	675	682	ν_s(CSC)A′DMSO bonded	ν_{10}
695	695	695	ν_a(CSC)A″DMSO free	ν_{22}
712	707	717	ν_a(CSC)A″DMSO bonded	ν_{22}
748	748	748	$2\delta(CCN)CH_3CN$	$2\nu_8$
917	917	917	$\nu(C–C)CH_3CN$	ν_4
928	931	931	$r(CH_3)$A″DMSO[b]	ν_9
			$\nu_s(ClO)$ ClO_4^-	ν_1
956	956	956	$r(CH_3)$A′DMSO[b]	ν_{21}
1060	1060	1060	ν(SO)A′DMSO[b]	ν_7
1372	1372	1373	$\delta_s(HCH, HCN)CH_3CN$	ν_3
1417	1418	1418	$\delta_s(CH_3)$A′DMSO[b]	ν_4
			$\delta_a(CH_3)$A″DMSO[b]	
1446	1446	1446	$\delta_a(HCH)CH_3CN$	ν_6
2251	2252	2252	$\nu(C–N)CH_3CN$	ν_2
2291	2291	2291	CH_3CN	$\nu_3 + \nu_4$
2920	2920	2920	$\nu_s(CH_3)$A′ and A″DMSO[b]	ν_3, ν_{16}
2941	2941	2941	$\nu_s(C–H)CH_3CN$	ν_1
3004	3004	3004	$\nu_a(C–H)CH_3CN$	ν_5
			$\nu_s(CH_3)$A′DMSO[b]	ν_1, ν_2, ν_{14}, ν_{15}
			$\nu_a(CH_3)$A″DMSO[b]	

[a] See refs. 22, 24 and 25. [b] Vibrations of bonded and free DMSO molecules are too close to be separated.

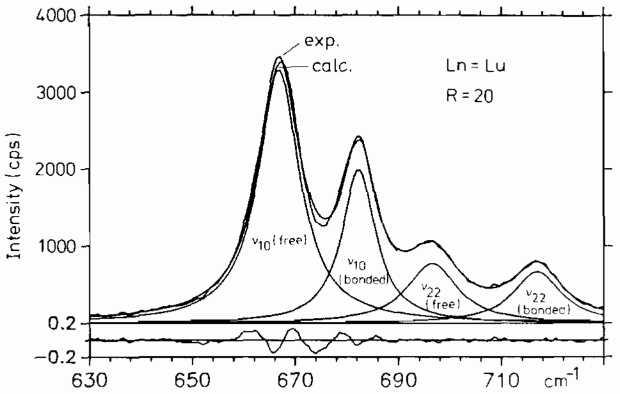

Fig. 4. Curve analysis of the Raman spectrum of $Lu(ClO_4)_3 \cdot 6.7DMSO$ 0.05 M in CH_3CN with $R = [DMSO]_t/[Ln]_t = 20$.

In conclusion, the identified transitions in both FT-IR and Raman spectra confirm the formation of inner-sphere complexes with DMSO. No additional bands can be assigned to outer-sphere complexes and no substantial variation in bandshape was observed upon variation of R between 7 and 20. This confirms that all the bonded DMSO molecules lie in the inner-coordination sphere and that they are more or less equivalent.

Coordination numbers

No interaction between Ln(III) and perchlorate ions or acetonitrile molecules was detected in the investigated solutions ($R = [DMSO]_t/[Ln]_t > 7$). Henceforth, the average coordination number (*CN*) of the lanthanide ions is equal to the average number n of bonded DMSO molecules. The ν_7 vibration was selected to determine the concentration of free DMSO in solution because it has a large absorption coefficient (*c*. 400 M^{-1} cm^{-1}). This advantage offsets the inconvenience of having to perform a curve-fitting analysis in the 980–1150 cm^{-1} spectral range. Another vibration suitable for quantitative analysis is the ν_{22} mode which is free from interferences, but its molar absorption coefficient is small (*c*. 40 M^{-1} cm^{-1}) and this vibration appears in a spectral range in which the IR detector used produces a more noisy signal.

The average coordination numbers obtained for three different compositions of the solutions, $R = 8$, 12 and 15, are summarized in Table 3 and Fig. 5. In order to obtain consistent data, the coordination numbers calculated for La solutions have been corrected for the dilution effect using the corresponding equilibrium constants (*vide infra*). For $R = 8$, the coordination numbers decrease regularly throughout the series. This situation reflects a gradual shift in the equilibria between eight-, seven- and six-coordinate solvates. The eight-coordinate species is favoured for the lighter Ln(III) ions while seven- and six-coordinate species predominate for the heavier lanthanides. For $R = 12$, the pattern is quite different. The *CN* values are almost constant between La and Eu and point to an equilibrium between eight- and nine-coordinate species. A discontinuity occurs between Eu and Gd where *CN* drops by one unit and then remains again practically constant down to Lu, with a slight tendency to decrease after Er. With respect to the data for $R = 8$, the average coordination number is larger by 1.1 unit for the first half of the series and by 0.7 unit for the second. In the presence of a larger excess of DMSO ($R = 15$), *CN* values become still larger. For La–Sm, ten-coordinate species are present in the solutions, while eight-coordinate solvates seem to prevail for Er–Lu. Two discontinuities are observed, between Sm and Eu and between Ho and Er, with a drop of 0.8 unit in *CN* each time. The ions Eu–Ho have the same *CN* values, *c*. 8.5, henceforth indicating that eight- and nine-coordinate solvates are predominant in their solutions. It is noteworthy that the average coordination number decreases by almost two units from La to Lu. For a given ion, the increase in *CN* when R is increased from 8 to 15 is usually monotonous (Fig. 6). The largest variation is observed for the lighter lanthanides (La–Sm) with an average change of almost 2 units between $R = 7$ and $R = 15$. For Eu–Lu, the difference is smaller and closer to about 1–1.2 units. Solutions with larger concentrations of DMSO, up to $R = 20$, were also studied, but *CN* data could not be extracted due to extensive spectral interferences between the vibrations of free and bonded DMSO molecules.

TABLE 3. Average coordination number *CN* (±0.4) for 0.05 M solutions of $Ln(ClO_4)_3 \cdot nDMSO$ in acetonitrile containing DMSO

Ln	$R^a = 8$	$R = 12$	$R = 15$
La[b]	7.8	8.7	9.7
Ce	7.4	8.4	–
Pr	7.4	8.7(9.0)[d]	9.9(9.7)[d]
Nd	7.7(7.9)[c]	8.7(8.9)[c, d]	9.5(9.3)[d]
Sm	7.4	8.6	9.3
Eu	7.5(7.3)[c]	8.8(8.9)[c]	8.5
Gd	7.2	7.7	8.5
Tb	7.2(7.5)[c]	7.6(8.8)[c]	8.5
Dy	7.0	7.8	8.3
Ho	7.2	7.9	8.6
Er	6.9	8.2(8.1[c], 8.2[d])	7.8(8.1)[c]
Tm	6.8	7.5	7.8
Yb	6.5	7.4	8.2
Lu	6.6	7.4	8.0

[a] $R = [DMSO]_t/[Ln]_t$. [b] Values recalculated for a 0.05 M concentration. [c] Values taken from ref. 26. [d] Values taken from ref. 23, in nitromethane.

A study of the interaction between four lanthanide perchlorates (Nd, Eu, Tb, Er) and DMSO was reported

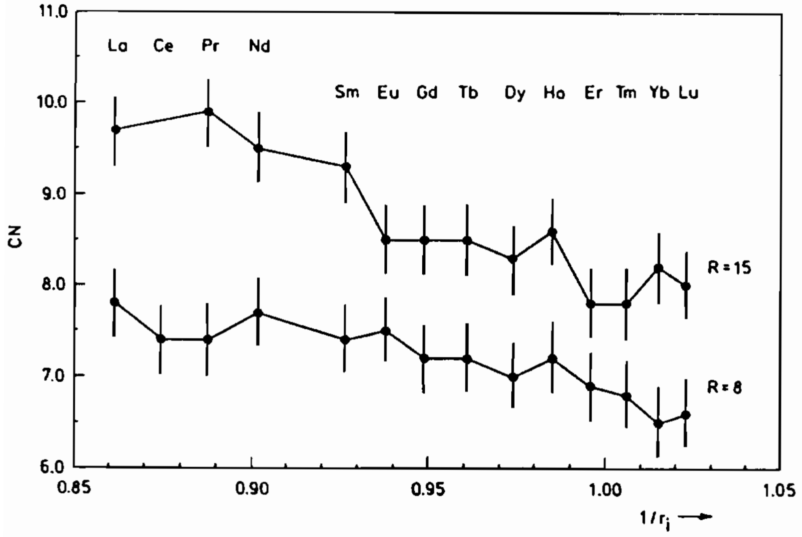

Fig. 5. Average coordination numbers of the Ln(III) ions in solutions of $Ln(ClO_4)_3 \cdot n$DMSO 0.05 M in CH_3CN vs. the reciprocal ionic radii for $CN=8$ [27]; $R=[DMSO]_t/[Ln]_t$.

by Mabillard and co-workers [10, 26] for R values ranging from 0 to 15. Coordination numbers were calculated from molar ratio plots using both the ν_7 and ν_{22} vibrations of bonded DMSO molecules. Our data are in excellent agreement with the *CN* values obtained by this method and with those obtained for Pr, Nd and Er solutions in nitromethane [23] (cf. Table 3).

Equilibrium constants

The formation of inner-sphere complexes between DMSO and Ln(III) ions may be described in terms of the following equilibria, with $x=6$–10:

$$[Ln(DMSO)_{x-1}]^{3+} + DMSO \overset{K_x}{\rightleftharpoons} [Ln(DMSO)_x]^{3+}$$

$$K_x = \frac{[Ln(DMSO)_x]^{3+}}{[Ln(DMSO)_{x-1}]^{3+} \cdot [DMSO]}$$

The apparent equilibrium constants K_x were evaluated according to both the mole fraction and Bjerrum's methods [28]. The K_x values reported in Table 4 are in line with the *CN* dependence upon the solvent composition. Log K_8 and log K_9 could be calculated for all the lanthanide ions; they behave similarly. Log K_9 decreases from 1 (La) to 0.4 (Lu). The most important change is observed between Eu (0.9) and Gd (0.5), consistent with the observed change in the average coordination number. Log K_8 decreases from 1.3 (Ce) to 0.6 (Lu); the value for La is somewhat larger (2.2), reflecting the tendency of this ion to display larger coordination numbers. Log K_{10} could be evaluated for La–Sm only; it varies from 0.9 to 0.3. In general, the above-calculated stability constants are 1 log-unit smaller than those calculated for the corresponding coordination numbers in lanthanide nitrate solutions ($x=6+n$) [17].

Conclusions

This systematic study of the interaction between DMSO and lanthanide perchlorates in anhydrous acetonitrile by FT-IR and Raman spectroscopy demonstrates that DMSO forms six-, seven-, eight-, nine- and ten-coordinate inner-sphere complexes with lanthanide ions. The average coordination number of a given ion increases when more donor molecules are introduced into the solution. The variation can amount up to 2 units for the lighter lanthanides. Changes of *CN* values along the Ln series are also evidenced and reflect the displacement of equilibria between these differently coordinated species. As expected, the coordination number decreases regularly with increasing Z, but when a significant excess of DMSO is added ($R>8$), marked differences appear at some points in the series. A 'break' of *c.* 1 unit is observed around the middle of the series and other significant, although smaller, variations appear around Nd and Er (*c.* 0.5 unit).

Similar results have been reported for solutions of lanthanide nitrates in anhydrous acetonitrile containing DMSO [17]. In these systems, the three nitrate ions are bonded in a bidentate fashion and the coordination number is $CN=6+n$, where n is the average number of bonded DMSO molecules. Coordination numbers ranging from 10 to 8 have been observed, and the overall conclusions of this study are similar to those drawn above. The coordination numbers evaluated for the nitrate solutions are, however, somewhat larger than those reported in this study. This may be explained

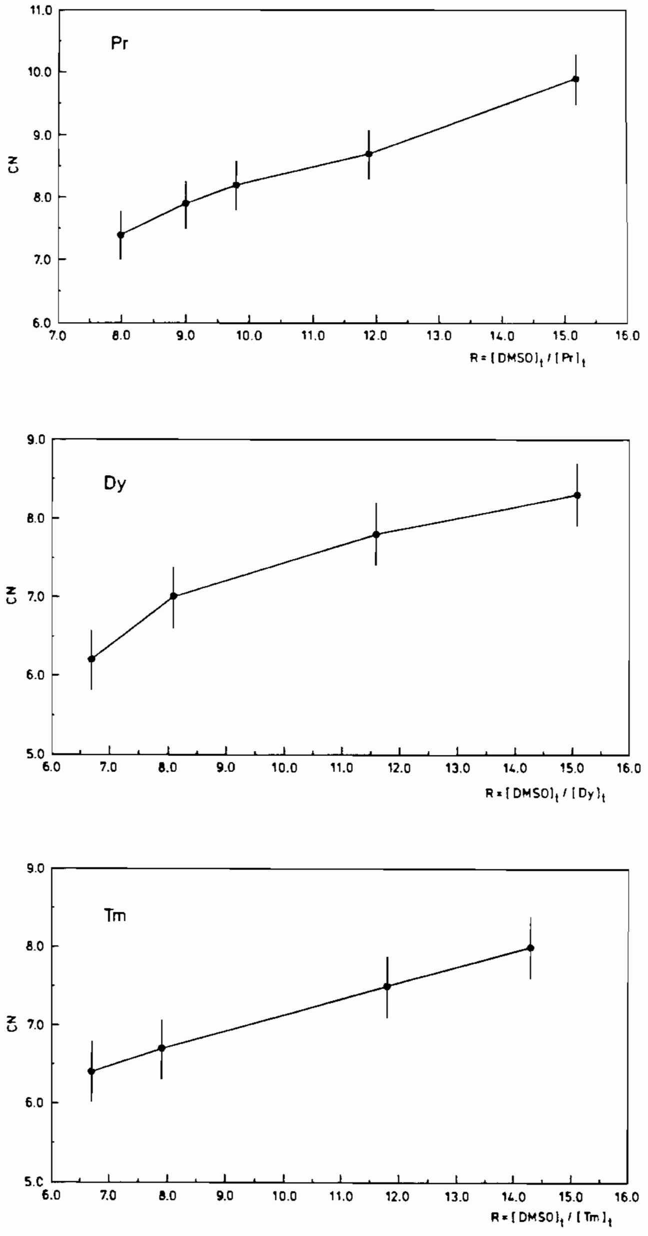

Fig. 6. Average coordination numbers of Ln(III) ions in solutions of $Ln(ClO_4)_3 \cdot n$DMSO 0.05 M in CH_3CN vs. $R = [DMSO]_t/[Ln]_t$.

TABLE 4. Apparent equilibrium constants log K_8, log K_9 and log K_{10} (± 0.2) (see text for an explanation)

Ln	log K_8	log K_9	log K_{10}
La[b]	2.2	1.0	0.9
Ce	1.3	0.7	0.4
Pr	1.4	1.0	0.6
Nd	2.0	0.9	0.6
Sm	1.5	0.8	0.3
Eu	1.6	0.9	
Gd	1.0	0.5	
Tb	0.9	0.5	
Dy	0.9	0.4	
Ho	0.9	0.4	
Er	1.0	0.5	
Tm	0.7	0.3	
Yb	0.6	0.4	
Lu	0.6	0.4	

by the occurrence of larger steric effects when the first coordination sphere is filled with DMSO molecules only. In both nitrate [17] and perchlorate solutions, the electrostatic interaction between Ln(III) and DMSO increases monotonously with increasing Z. On another hand, vibrational data do not evidence large inequivalencies between the coordinated DMSO molecules, so that we may interpret the variations in coordination numbers as follows. When excess DMSO is added, the inner coordination sphere of the Ln(III) ion expands to accept an additional donor molecule, resulting in a slightly weaker Ln–DMSO interaction (cf. Table 1). The thermodynamic stabilities of the species $[Ln(DMSO)_x]^{3+}$ and $[Ln(DMSO)_{x+1}]^{3+}$ are close, as demonstrated by the small values calculated for log K_{x+1}. The electronic density on the trivalent ions increases with Z, therefore they are in situations in which the expansion of the inner-coordination sphere leads to species with too small a free energy to be stable enough and for which the equilibrium involving two differently coordinated species is substantially shifted to favour the species with the smallest coordination number. Therefore, the observed breaks in coordination numbers along the series are second-order effects resulting from a subtle interplay between electronic and steric effects. A similar situation seems to prevail for aquo ions [4] for which it has been demonstrated that the difference in free energy between ennea- and octa-coordinated solvates is rather small [29].

In conclusion, this and previous studies [17, 18] establish on the basis of systematic data that the first-coordination sphere of the lanthanide ions is easily adjustable to the environment in which these ions are exposed. This explains the versatility and adaptability of these elements when they are used as spectroscopic probes in complex biological or environmental systems [30], as well as their chemical properties in organometallic reactions [31].

Acknowledgements

This research is supported by grants from the Swiss National Science Foundation. We thank Dr L. Zekany for designing the curve-fitting program and Mr D. Baumann for technical assistance in recording the FT-IR spectra.

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