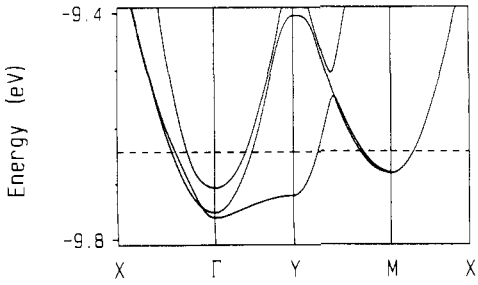
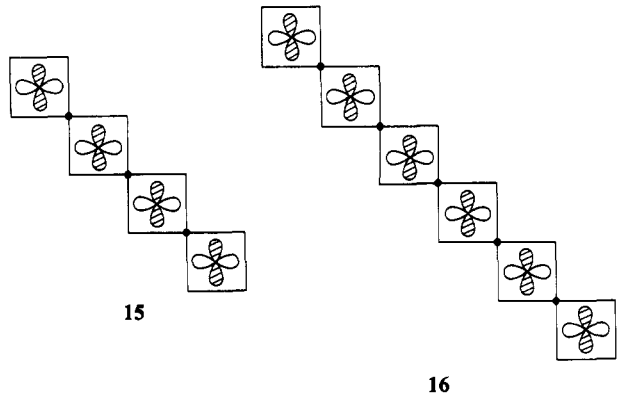


Figure 5. Dispersion relations of the bottom portion of the t_{2g}-block band calculated for the W_6O_{22} layer of $(WO_3)_6(WO_3)_6(PO_2)_4$. The dashed line refers to the Fermi level corresponding to 2 d electrons per unit cell.



almost equally. Lack of strong bridging p-orbital contributions also makes those three bands close in energy at Γ (from the viewpoint of the overall t_{2g}-block band dispersions).

In the perovskite-type W–O layers, the W atoms interact via the W–O–W bridges. Thus, a d-block band orbital in which contributions of the bridging oxygen p orbitals are absent would have an energy close to that of the atomic d level. This should be the case regardless of how many WO_6 octahedra per unit cell are used to form a perovskite-type W–O layer. For example, band a of the W_4O_{16} layer is constructed from the orbital pattern **15** (in each W_4O_{18} step **2**). Likewise, the corresponding band of the W_6O_{22} layer is constructed from the orbital pattern **16** (in each W_6O_{26} step **5**). Since **15** and **16** have similar energies and similar nodal patterns, the resulting bands a of the W_4O_{16} and W_6O_{22} layers should be similar. According to the same reasoning, it is predicted that the bottom three t_{2g}-block bands of the W_4O_{16} layer should be similar to those of the W_6O_{22} layer or any other perovskite-type W–O step layer. Since the W–O step layer of the MPTB phases have between 2 and 4 d electrons per unit cell, it is also predicted that all MPTB phases should have both 1D and 2D metallic bands. We have confirmed these predictions for all MPTB phases with known crystal structures. As a representative example, we show in Figure 5 the dispersion relations of the t_{2g}-block bands calculated for the W_6O_{22} step layer in $(WO_3)_6(WO_3)_6(PO_2)_4$.

Concluding Remarks

Our study shows that all MPTB phases should have both 1D and 2D metallic bands, regardless of the difference in their W–O layer thickness. This remarkable similarity originates from the fact that the W–O layers of the MPTB have between 2 and 4 d electrons per unit cell, and thus, only the bottom three of the t_{2g}-block bands can be partially filled due to their overlapping. Our sudy also shows that predictions of a bond valence sum analysis can be erroneous when the extents of metal–oxygen···metal bond alternations do not have a wide variation, as in the case of the MPTB phases.

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Evidence for a Coordination Number Change along the Lanthanide Series: FT-IR Investigation of the Solvates $[Ln(NO_3)_3(DMSO)_n]$ in Anhydrous Acetonitrile[1]

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The interaction between lanthanide nitrates and dimethyl sulfoxide (DMSO) has been studied in anhydrous acetonitrile by FT-IR difference spectra. If $R = [DMSO]_t/[Ln(III)]_t$ is kept low enough (typically <9), nitrate ions do not dissociate and remain bonded in a bidentate fashion. A quantitative study of the ν_7(S–O) and ν_{22}(C–S) stretching modes has been performed for solutions generally 0.05 M in Ln(III), with Ln = La (0.012 M), Ce, Pr, Sm, Gd, Dy, Ho, Tm (0.029 M), Yb, and Lu, and R between 0 and 6. Average coordination numbers CN of the Ln(III) ions are reported for various compositions of the solutions. The data for $R = 6$, along with the previously published data for Nd, Eu, Tb, and Er, point to a large variation along the series, from 10.2 ± 0.3 for La to 8.4 ± 0.3 for Lu. La is 10-coordinate, and the main changes occur between Sm and Gd (0.6 unit) and between Er or Tm and Yb (0.6 unit). The coordination numbers depend upon the DMSO concentration, the data obtained for $R = 6$ being larger by approximately 0.5 unit than the coordination numbers determined for $R = 3$. Data for $R = 3$ confirm the CN change in the Pr–Eu region, but the variation is smaller; the small change between Gd and Lu occurs very gradually. For $R = 2$–6, there is an equilibrium between 9- and 10-coordinate species for the lighter lanthanides and between 8- and 9-coordinate species for the intermediate and heavier ions. Apparent stability constants have been calculated; they vary between $\log K_{10} = 2.2 \pm 0.1$ (La) to 0.9 ± 0.1 (Sm) and $\log K_9 = 1.8$ ■ 0.1 (Eu) to 1.0 ± 0.1 (Lu).

Introduction

The 14 trivalent f-block ions, from Ce(III) to Lu(III), plus La(III), herein denoted Ln(III) ions, form an extended series of cations with the same formal charge and with similar chemical properties. The $4f^n5s^25p^6$ electronic configuration ensures that the bonding and stereochemistry of Ln(III) complexes and solvates are largely determined by both the predominantly ion–dipole bonding interaction between Ln(III) and the ligands and the steric repulsion between coordinated ligands. In fact, coordination numbers ranging from 3 to 14 have been reported in the solid state.[3,4] Many aspects of the coordination chemistry of these ions

(1) FT-IR and Fluorometric Investigation of Rare-Earth and Metal Ion Solvation. 9. Part 8: see ref 17.
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in solution remain unclear, mainly because of the presence of equilibria between ions with different coordination numbers and/or with same coordination number but with different coordination polyhedra.[3,5a] In particular, the possibility of a change in hydration number within the 15-element series as the ionic radius decreases monotonously from La(III) to Lu(III) has long been debated[5] and could only be ascertained recently by making use of sophisticated instrumentation.[6] In non-aqueous solutions, the study of solvation processes has proved more tractable, especially in solvents with large donor numbers such as dimethylformamide (DMF).[5,7] However, due to the difficulty of working under anhydrous conditions, few papers report the determination of Ln coordination numbers in organic solvents.

In our laboratory, we have initiated a systematic investigation of the coordination numbers of trivalent lanthanide ions and of their interaction with various anions, both in anhydrous organic solvents and in mixed solvents. We have used UV–visible absorption spectroscopy and luminescence techniques to elucidate the complexation ability of Nd,[8] Eu,[9–13] and Tb[14] toward nitrate and several weak and strong organic donors. We have also addressed the problem of anion complexation in methanol, with ^{139}La NMR spectroscopy.[15] Finally, utilizing FT-IR techniques, we have proved that some degree of inner-sphere association occurs between perchlorate anions and Nd, Eu, Tb, and Er ions in anhydrous acetonitrile,[11,16] and we have analyzed the interaction between these ions and both nitrate and dimethyl sulfoxide (DMSO).[12,17]

In this paper, we extend our previous work on the interaction between $Ln(NO_3)_3$ (Ln = Nd, Eu, Tb, Er) and DMSO in anhydrous acetonitrile (MeCN)[12,17] to all the remaining members of the Ln series, with the exception of Pm. The reported coordination numbers represent the first consistent series of such data for Ln(III) ions in organic solution. Apparent stability constants for the coordination of DMSO are also evaluated and discussed.

Experimental Section

Reagents. Hydrated lanthanide nitrates were prepared by dissolving 5 mmol of lanthanide oxide (99.9 or 99.99%, Glucydur or Research Chemicals) in 28–29 mmol of concentrated HNO_3 (Merck, analytical grade). The mixture was stirred for 1–2 h at 40–50 °C and filtered to remove the excess oxide before evaporating the solution to dryness. The collected nitrate salt was dried over KOH and then heated in vacuo (10^{-2} mmHg) for 2–3 days at 70–80 °C, yielding $Ln(NO_3)_3 \cdot xH_2O$, with x = 3–4. Final dehydration was achieved by stepwise heating under high vacuum (10^{-6} mmHg) with the following final temperatures (°C): 220 (La), 180 (Ce), 210 (Pr), 190 (Sm), 170 (Gd), 160 (Dy, Ho), and 150 (Tm, Yb, Lu). Absence of water in anhydrous nitrates was verified by IR spectroscopy.

Acetonitrile (Fluka, puriss) was treated with CaH_2 and P_4O_{10} and distilled twice. The collected fractions contained between 20 and 30 ppm of water (as measured by Karl Fischer titration using a Mettler DL-18 apparatus) and were stored over 3-Å molecular sieves in a glovebox. DMSO (Fluka, spectroscopic quality) was dried over 3-Å molecular sieves. Solutions were prepared in a glovebox, under inert atmosphere (N_2) with less than 5 ppm of water. If necessary, traces of insoluble oxynitrates $LnONO_3$ were filtered. Lanthanide concentration (M) was determined by complexometric titration with Titriplex III (Merck) in the presence of urotropine and xylenol orange: 0.012 (La), 0.049 (Ce), 0.050 (Pr, Sm, Gd, Ho, Lu), 0.048 (Dy), 0.029 (Tm), and 0.051 (Yb). The low concentration of the La solution is due to solubility problems.

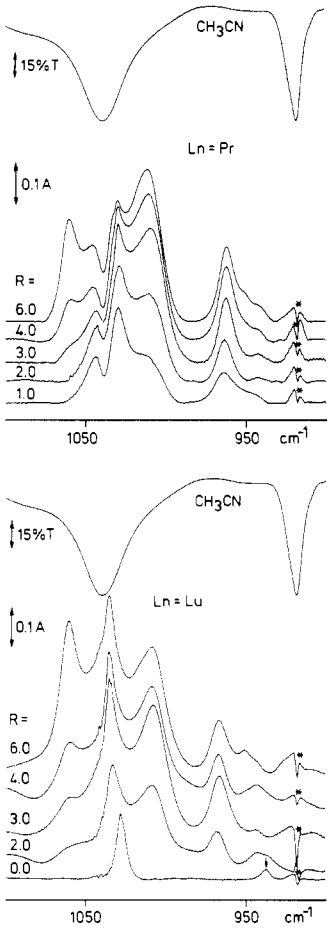

Figure 1. DMSO vibrations of solutions of 0.05 M $Ln(NO_3)_3$ in MeCN containing DMSO. The upper trace represents the spectrum of bulk MeCN in transmission units. $R = [DMSO]_t/[Ln]_t$. Stars denote incomplete compensation of the solvent, and the arrow points to the ν_4 mode of bound MeCN.

Spectroscopic Measurements. FT-IR difference spectra[11] were recorded with an IFS-113v Bruker spectrometer. The data acquisition and handling system included a 16-bit converter, a 256-Kbyte 24-bit Aspect 3000 computer, a floppy-disk unit, and a 160-Mbyte hard disk (Hitachi). Calibration of the spectrometer was performed as previously described.[11] The mid-IR spectra were measured under the following conditions: N_2 purge, 1 cm^{-1} bandpass, 4 points/spectral element, trapezoidal (4-point) apodization, 500 scans. Liquid cells were filled in the glovebox. The optical path was between 23 and 100 μm; the cell thickness was determined before each measurement by the interference fringe method,[18] and the observed absorbances were corrected accordingly. Silver chloride windows were used despite their large refractive index to avoid adsorption problems. The reported data are averages of several measurements performed on at least two independently prepared solutions.

Raman spectra were measured with a Spex Ramalog-4 instrument (Kr laser).

Results

FT-IR Difference Spectra. Lanthanide nitrates behave as nonelectrolytes in anhydrous acetonitrile, with molar conductivities between 7 (Er) and 15 (Nd) $\Omega^{-1} \cdot cm^2 \cdot M^{-1}$.[19] FT-IR difference

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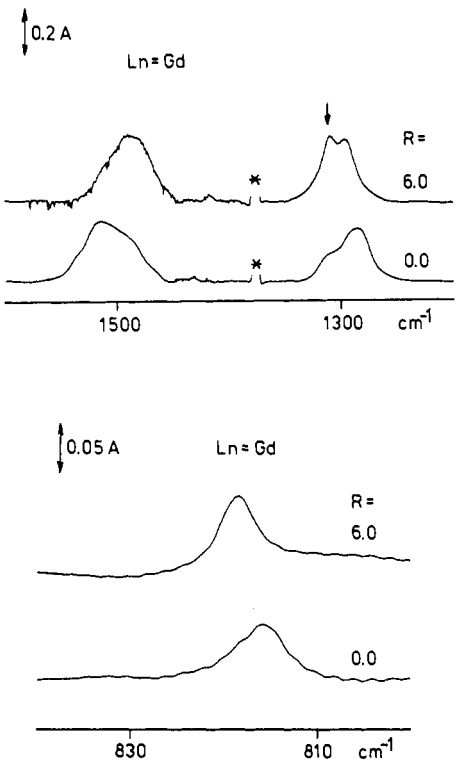

Figure 2. Nitrate vibrations of 0.05 M $Gd(NO_3)_3$ solutions in MeCN containing DMSO. $R = [DMSO]_t/[Ln]_t$. The star denotes an incomplete compensation of the solvent. The arrow points to a DMSO vibration.

spectra confirm this finding in displaying absorptions from bonded nitrate ions only, for all the Ln solutions. Vibrational modes from coordinated MeCN molecules are also observed. When DMSO is added to these solutions, it quantitatively displaces the MeCN molecules out of the inner-coordination sphere, and absorptions from bonded DMSO molecules appear in the spectra (Figure 1). Several of the 24 fundamental modes of DMSO are affected very little by the complexation with the metal ion or interfere with other absorptions (bonded nitrate at 1300–1500 cm^{-1} and acetonitrile at 2800–3000 cm^{-1}). The other modes are significantly shifted with respect to the absorptions of bulk DMSO. Data are reported in Table I, with vibrational modes labeled according to C_s symmetry.[20] The largest shift occurs for the S–O stretch ν_7 (ca. 50 cm^{-1}) and this bathochromic effect is consistent with a coordination through the O atom. The asymmetric C–S stretch ν_{22} is blue-shifted by about 20 cm^{-1}. These shifts remain fairly constant over the Ln series and show little variation with the DMSO concentration. As increasing amounts of DMSO are added to the solutions, absorptions of free DMSO appear, when $R = [DMSO]_t/[Ln(III)]_t > 3$ for the lighter lanthanides and when $R > 2.5$ for the heavier ions. Simultaneously, the absorptions of coordinated MeCN molecules disappear when $R > 4$ and $R > 3$, respectively. This points to the presence of equilibriá involving species with different coordination numbers. Since no significant change occurs in the shifts of the S–O and C–S stretches between $R = 2$ and 6, the Ln(III)–DMSO interactions are, however, similar in these species.

Nitrate vibrations are reported in Table T1 (supplementary material), and typical examples are given in Figure 2. Their frequencies correspond to those assigned to bidentate nitrate ions with a C_{2v} local symmetry:[13] $\nu_1(A_1)$, $\nu_4(B_2)$, $\nu_2(A_1)$, $\nu_6(B_1)$, and $\nu_3(A_1)$ at ca. 1500, 1295, 1030, 820, and 735 cm^{-1}, respectively; $\nu_5(B_2)$ at 715 cm^{-1} was only found in the Raman spectra. The assignment was confirmed by Raman polarization measurements on a 0.15 M Yb solution with $R = 6$: $\nu_2(A_1)$ and $\nu_3(A_1)$ were found

Table I. Observed Shifts, $\bar{\nu}$(coordinated) − $\bar{\nu}$(free) (±1 cm^{-1}), for Vibrations Assigned to Coordinated DMSO Molecules in $Ln(NO_3)_3$ Solutions 0.05 M in MeCN

vibration[a]	ν(DMSO),[b] cm^{-1}	$\bar{\nu}$(coordinated) − $\bar{\nu}$(free), cm^{-1}																					
		La[c]		Ce		Pr		Sm		Gd		Dy		Ho		Tm[d]		Yb		Lu	
		R[e] = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0	R = 2.0	R = 6.0
ν_{22}: ν(CS)A″	697	19	15	22	18	19	18	19	18	20	20	22	21	20	19	21	20	22	20	21	21
ν_9: $r(CH_3)$A″	927	14	17	13	15	15	15	15	16	16	17	16	16	17	16	16	17	16	16	17	16
ν_{21}: $\nu(CH_3)$A′	950	12	12	13	11	13	12	14	13	14	13	15	15	16	15	16	16	17	15	18	17
ν_7: ν(SO)A′	1060[f]	−49	−47	−52	−48	−50	−50	−53	−52	−52	−50	−52	−52	−52	−52	−52	−52	−52	−54	−51	−51
ν_6: $\delta(CH_3)$A′	1309	−4	−2	−5	−2	−5	−2	−4	−3	−5	0	−2	1	−1	2	−2	4	−3	2	−2	4

[a] The assignments are made on the basis of a C_s symmetry. [b] Vibrational frequencies of free DMSO in a 0.3 M solution in MeCN. [c] 0.012 M. [d] 0.029 M. [e] $R = [DMSO]_t/[Ln]_t$. [f] Interferes with ν_{20}: $r(CH_3)$A″.

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Table II. Splitting of Nitrate Vibrations $\tilde{\nu}_1$ and $\tilde{\nu}_4$ (cm^{-1}) in 0.05 M $Ln(NO_3)_3$ Solutions in MeCN Containing DMSO

Ln	$\tilde{\nu}_1 - \tilde{\nu}_4$ $R = 1^a$	$\tilde{\nu}_1 - \tilde{\nu}_4$ $R = 6^a$	$\Delta(\tilde{\nu}_1 - \tilde{\nu}_4)$ ($R = 1$, $R = 6$)
La[b]	187	180	7
Ce	188	178	10
Pr	195	184	11
Sm	205	188	17
Gd	210	188	22
Dy	214	188	26
Ho	215	188	27
Tm[c]	210	191	19
Yb	210	191	19
Lu	215	193	22

[a] $R = [DMSO]_t/[Ln]_t$. [b] 0.012 M. [c] 0.029 M.

Table III. Observed Shifts $\tilde{\nu}$(coordinated) − $\tilde{\nu}$(free) (± 1 cm^{-1}) for the $\tilde{\nu}_2$ and ($\tilde{\nu}_3 + \tilde{\nu}_4$) Modes of Coordinated Acetonitrile Molecules in 0.05 M $Ln(NO_3)_3$ Solutions in MeCN Containing DMSO[a]

Ln	$\Delta(\tilde{\nu}_2)$ $R = 0^b$	$\Delta(\tilde{\nu}_2)$ $R = 2^b$	$\Delta(\tilde{\nu}_3 + \tilde{\nu}_4)$ $R = 0^b$	$\Delta(\tilde{\nu}_3 + \tilde{\nu}_4)$ $R = 2^b$
Ce	23	22	14	13
Pr	24	22	13	12
Nd[c]	24	23	15	14
Sm	26	25	14	15
Eu[c]	27	26	16	15
Gd	28	27	17	15
Tb[c]	28	27	17	15
Dy	29	28	18	17
Ho	30	29	19	18
Er[c]	30	29	19	17
Tm	31	30	19	18
Yb	33	31	20	19
Lu	33	31	21	19

[a] The La solution was too diluted to be measured. [b] $R = [DMSO]_t/[Ln]_t$. [c] Data from refs 11 and 19.

to be polarized while $\nu_4(B_2)$ and $\nu_5(B_2)$ were not polarized; $\nu_1(A_1)$ and $\nu_6(B_1)$ were not observed due to interferences. All the nitrate vibrations undergo a slight red shift upon addition of DMSO, and the absorption bands become more symmetrical, as already observed for Nd, Eu, Tb, and Er.[17] No absorption from ionic nitrate was observed for any Ln ion, even at the largest concentrations in DMSO ($R = 6$). We have previously shown by luminescence measurements on Eu-containing solutions that nitrate starts dissociating only when $R > 9$.[12] The ν_1–ν_4 splitting reflects the magnitude of the Ln(III)–nitrate interaction. Two sets of data are given in Table II, for $R = 1$ and 6. The observed splittings for $R = 1$ increase substantially from 187 cm^{-1} (La) to 210–215 cm^{-1} (Gd–Lu), that is with increasing charge density on the Ln ions. On addition of more DMSO ($R = 6$), the splittings decrease for all the Ln ions, but this effect is larger for the heavier lanthanides. We note that the latter splittings are similar to those observed for $[Ln(NO_3)_5]^{2-}$ anions in MeCN solutions.[19] Examination of crystal structure data available on $[Ln(NO_3)_5]^{2-}$ anions and $[Ln(NO_3)_3(DMSO)_n]$ solvates (e.g. Ln = Er[21]) reveals that the average Ln–O(NO_3) distances are indeed the same in both species, the average Ln–O(DMSO) distances being much shorter.

In lanthanide nitrate solutions, four vibrational modes of acetonitrile are substantially blue-shifted upon complexation:[11,19] ν_8(CCN), ν_4(C—C), ν_2(C≡N), and the combination ν_3(HCN) + ν_4(C—C), at ca. 395–405 (+20 to +25), 935–940 (+20), 2275–2285 (+23 to +33), and 2305–2315 (+14 to +21) cm^{-1}, respectively. The latter two vibrations have a sizable intensity and relevant data are given in Tables III and T2 (supplementary material) while a typical spectrum is displayed in Figure 3. The shifts increase monotonously by 50% in going from Ce to Lu, and they become slightly, but consistently, smaller when DMSO is added ($R = 2$). In line with a simple explanation based on the variation of electron density on the lanthanide ion, we note that the corresponding shifts for perchlorate solutions[11,19,22] are somewhat larger (ca. 10%), but follow the same trends.

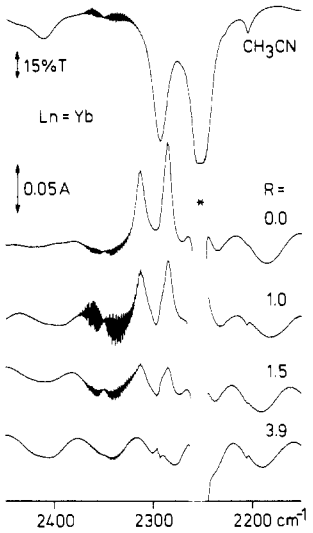

Figure 3. Acetonitrile vibrations of 0.05 M $Yb(NO_3)_3$ solutions in MeCN containing DMSO. $R = [DMSO]_t/[Ln]_t$. The star denotes an incomplete compensation of the solvent. The fine structure around 2350 cm^{-1} arises from traces of CO_2 present in the spectrometer.

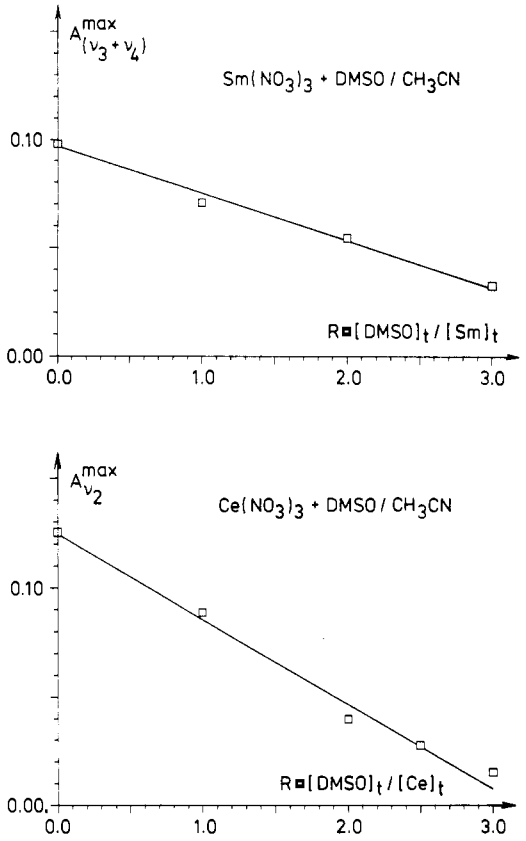

Figure 4. Absorbances of the ν_2 and $\nu_3 + \nu_4$ vibrations of bound acetonitrile in 0.05 M $Ln(NO_3)_3$ solutions in MeCN containing DMSO. $R = [DMSO]_t/[Ln]_t$.

When the absorbances at the maximum of the ν_2 and $\nu_3 + \nu_4$ bands are plotted against R (Figure 4), straight lines are usually obtained up to $R = 2$ or 3, indicating a 1:1 replacement of MeCN

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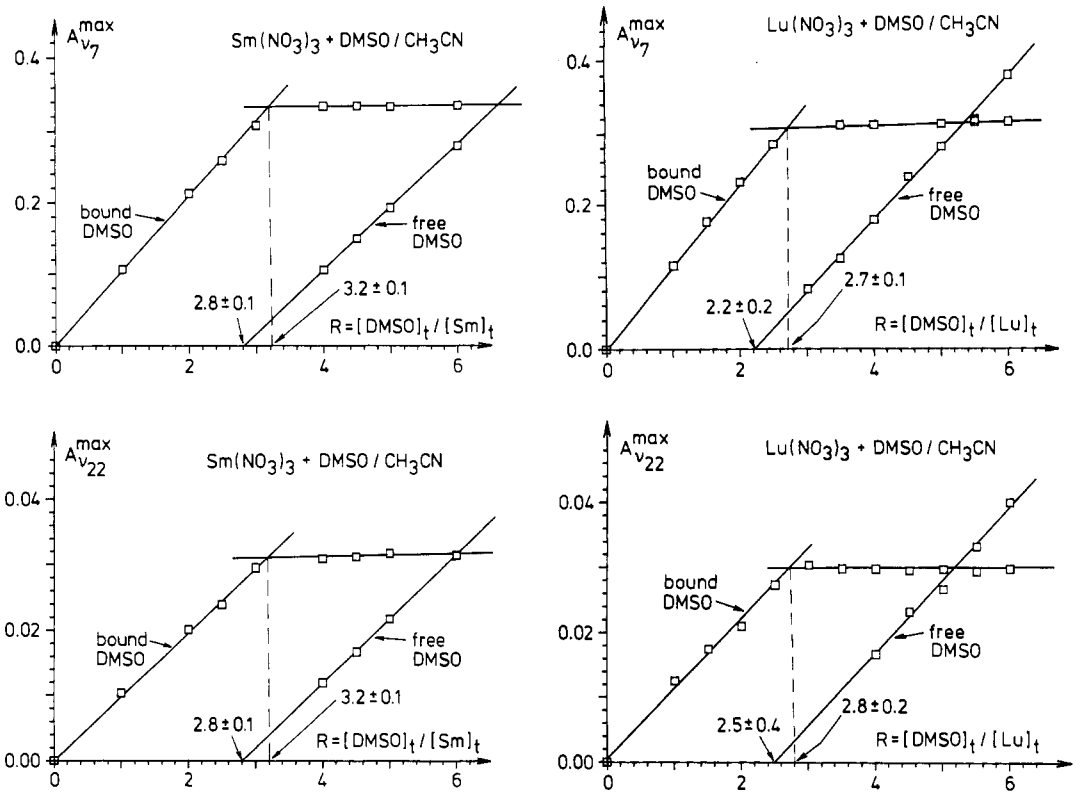

Figure 5. Absorbances at the maxima of the bands assigned to the ν_7(SO) and ν_{22}(CS) modes of bonded and free DMSO in 0.05 M Ln(NO$_3$)$_3$ solutions in MeCN containing DMSO.

by DMSO molecules. Some graphs are nonlinear for larger R values pointing to equilibria between differently coordinated species. It is noteworthy that the intensity of the absorption bands is considerably enhanced upon complexation, the molar absorption coefficients increasing from 38 (ν_2) and 8.4 ($\nu_3 + \nu_4$) L·mol^{-1}·cm^{-1} in bulk acetonitrile[19] to approximately 140–160 and 90–110 L·mol^{-1}·cm^{-1}, respectively.

Coordination Numbers. Since the solvated species are [Ln(NO$_3$)$_3$(DMSO)$_n$] with the three nitrate ions bonded in a bidentate fashion, the coordination number of the Ln(III) ion is CN = 6 + n. To determine the average number of coordinated DMSO molecules per Ln(III) ion, we have monitored two vibrations, ν_7 and ν_{22}. The first vibration, in the spectral range 980–1070 cm^{-1}, is strong but is a composite band (cf. ref 12) and interferes with both ν_2(NO$_3$), and ν_7(MeCN). Quantitative work on the absorption bands corresponding to bonded and free DMSO molecules is nevertheless feasible because (i) they appear at both ends of the spectral range, (ii) the solvent band can be removed by subtraction since complexation induces only a very small shift of this vibration, and (iii) the nitrate band is narrow enough to create a minimum perturbation. The maximums of ν_7 at ca. 1010 (bonded) and 1060 (free) cm^{-1} were therefore selected for quantitative work. Curve resolution procedures similar to those performed for perchlorate solutions[12] did not improve the quality of the data and were not used. The other vibration, ν_{22}, is free from interferences but its molar absorption coefficient is small and it appears in a spectral range in which our detector produces a noisy signal, leading to less precise quantitative measurements. The results obtained with data from the two spectral ranges were always in excellent agreement, usually to ±5–10%. This figure sets an upper limit on our precision. Since the number of bonded DMSO molecules oscillated between 2 and 3, this means that our overall accuracy on the coordination numbers is between ±0.2 and ±0.3. The average number of bonded DMSO molecules was calculated from the total DMSO concentration and the free DMSO concentration. The latter was assessed by means of calibration curves: $\epsilon(\nu_7) = 420 \pm 8$ and $\epsilon(\nu_{22}) = 42 \pm 4$ L·mol^{-1}·cm^{-1} (Figure F1, supplementary material).

Plots of the absorbance of the two selected vibrations vs R are shown in Figures 5 and F2 (supplementary material). The curves increase linearly up to $R = 2$ (heavier ions) or 3 (lighter ions), and level off for $R > 4$. Intercepts of the two straight segments usually occur for fractional values of R. Extrapolating to zero the lines depicting the variation in absorbance of free DMSO usually yields intercepts at smaller R values. This points to the presence of equilibria:

$$[Ln(NO_3)_3(DMSO)_{n-1}] + DMSO \overset{K_x}{\rightleftharpoons} [Ln(NO_3)_3(DMSO)_n] \quad (I)$$

For lighter lanthanide ions, $n = 4$, and depending upon R, a small percentage of species containing both DMSO and MeCN in their first coordination sphere may be present. For heavier lanthanide ions, $n = 3$ and most solutions contain both 8- and 9-coordinate species. This is in agreement with measurements made on solutions of comparable concentration in the isolated adducts [Ln(NO$_3$)$_3$(DMSO)$_n$] ($n = 4$ for La–Tb and $n = 3$ for Dy–Lu). All these solutions display bands attributable to free DMSO, and the

Table IV. Average Number of Coordinated DMSO Molecules per Lanthanide Ion (N, ±0.3) and Average Coordination Number (CN, ±0.3)[a] of these Ions in 0.05 M Ln(NO$_3$)$_3$ Solutions in MeCN Containing DMSO

	$R = 3^b$			$R = 4^b$			$R = 6^b$		
Ln	N^c	N^d	CN^c	N^c	N^d	CN^c	N^c	N^d	CN^c
La	3.0		9.3[e]	3.4		9.4	4.2		10.2
Ce	3.0	3.0	9.3[e]	3.1	3.0	9.1	3.7	3.7	9.7
Pr	3.0	3.0	9.2[e]	3.3	3.3	9.2	3.9	4.2	9.9
Sm	3.0	3.0	9.2[e]	3.2	3.3	9.2	3.6	3.5	9.6
Gd	2.7	2.5	8.7	2.8	2.6	8.8	3.0	2.7	9.0
Dy	2.6	2.9	8.6	2.8	3.2	8.8	3.0	3.0	9.0
Ho	2.4	2.4	8.4	2.5	2.7	8.5	3.0	3.0	9.0
Tm	2.2	2.3	8.2	2.3	2.3	8.3	2.8	2.7	8.8
Yb	2.4	2.5	8.4	2.3	2.7	8.3	2.3	2.8	8.3
Lu	2.2	2.4	8.2	2.3	2.4	8.3	2.4	2.4	8.4

[a] Coordination number = 6 + N, calculated by using data from the ν_7 vibration. [b] R = [DMSO]$_t$/[Ln]$_t$. [c] Calculated by using the ν_7(DMSO) absorption. [d] Calculated by using the ν_{22}(DMSO) absorption. [e] The inner coordination sphere contains on average 0.3 or 0.2 MeCN molecules.

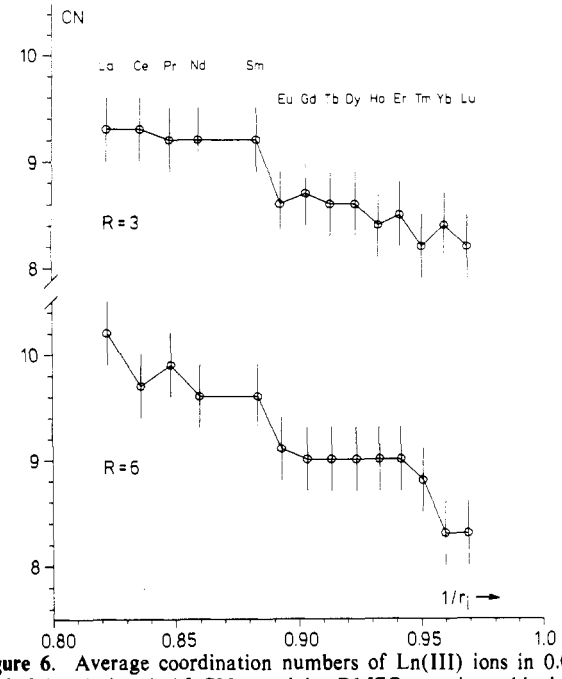

Figure 6. Average coordination numbers of Ln(III) ions in 0.05 M $Ln(NO_3)_3$ solutions in MeCN containing DMSO vs reciprocal ionic radii (values taken for CN = 9[23]). $R = [DMSO]_t/[Ln]_t$. Data for Nd, Eu, Tb, and Er are from ref 17.

calculated concentration of the latter is in agreement with the above-reported results.

Coordination numbers for three different compositions of the solutions are reported in Table IV and graphically represented in Figure 6, along with the numbers previously determined for Nd, Eu, Tb, and Er.[17] For $R = 6$, the CN values constantly decrease from 10.2 for La to 8.4 for Lu, which represents a change of almost 2 units. A closer look at the curve indicates that La has an inclination for 10-coordination, Ce–Sm are intermediate, between 10 and 9, and Eu–Tm have a preference for 9-coordination, while Yb and Lu tend toward 8-coordination. It is likely that the La solutions, which were more diluted than the others, contain a sizable amount of 11-coordinated species, but our data are not precise enough to establish this fact; 11-coordination is well documented for La–nitrato complexes.[24] The interesting finding is that coordination number changes occur in at least two regions of the Ce–Lu series, namely between Sm and Gd (0.6 unit) and between Er or Tm and Yb (0.6 unit). Also, the average coordination numbers increase with increasing concentration of DMSO. The data for $R = 3$ are less differentiated, with a total variation between La and Lu of 1.1 units. They confirm the clear-cut change in coordination number between Sm and Eu described above, but La behaves similar to the other lighter lanthanide ions. The CN change between Eu (8.6) and Lu(8.2) occurs very gradually and is at the significance limit. For this solvent composition, Ln(III) ions can therefore be divided into two classes: La–Sm (CN = 9) and Gd–Lu (with the coordination number intermediate between 9 and 8). Finally, we note that the difference in CN between $R = 3$ and $R = 6$ is approximately constant and equal to 0.5 ± 0.1 from Ce to Tm. It is larger for La and vanishes for Yb and Lu. These trends may be interpreted as the result of the interplay of steric and electrostatic effects.

The apparent equilibrium constants K_x defined by eq 1, with $x = 6 + n$, are reported in Table V. They are relatively low, in line with the CN dependence upon the solvent composition; log K_{10} values decrease from 2.2 (La) to 0.9 (Sm), and similarly, log K_9 values decrease from 1.8 (Gd) to 1.0 (Lu). That is, the small log K_x values could mean that the "preferred" coordination numbers of the Ln ions is about 9 for the larger ones and 8 for the smaller ones. This would parallel the recent findings for aqueous solutions, for which it has been shown that the hydration number decreases from 9 to 8.[6] The increase of CN by one unit is made possible by the strong donor properties of the DMSO molecule, which is known to have a larger affinity for Ln(III) ions than water.[12]

Table V. Apparent Equilibrium Quotients log K_9 and log K_{10} (M^{-1})[a]

Ln	log K_x $R = 3$[b]	$R = 4$[b]	$R = 6$[b]	av
		log K_{10} (±0.1)		
La		2.2		2.2
Ce			1.7	1.7
Pr		1.0		1.0
Sm		0.7	1.0	0.9
		log K_9 (±0.1)		
Gd	1.7	1.9		1.8
Dy	1.5	1.9		1.7
Ho	1.2	1.3		1.3
Tm	1.0	1.2		1.1
Yb	1.1	0.9	0.9	1.0
Lu	0.9	0.9	1.1	1.0

[a] See text. [b] $R = [DMSO]_t/[Ln]_t$.

Discussion

The above data represent the first consistent series of coordination numbers determined in organic solution for the entire lanthanide series. They unambiguously point to a change in the average coordination number along the Ln series. In the presence of a relatively low concentration of the strong donor DMSO ($R = 3$), this change occurs approximately in the middle of the series (Eu), and we have two situations, one in which 9-coordinate species are predominant and the other in which 8-coordinate species are increasingly present. Higher average coordination numbers can be obtained for most ions (La–Tm) if the concentration of DMSO is increased ($R = 6$). In this case, two groups of ions seem to give rise to predominantly one solvate, La–Sm (CN = 10) and Eu–Tm (CN = 9), while Yb and Lu are intermediate with average CN's between 9 and 8.

Similar results have been reported for solutions of lanthanide perchlorates in acetonitrile containing DMSO (Ln = Nd, Eu, Tb, Er),[19] in particular with respect to the dependence of the average CN's on the DMSO concentration. The coordination numbers are, however, smaller: 9.1 for Nd and 8.0 for Er in the presence of a 2-fold excess of DMSO ($R = 20$). This may be traced back to the larger steric effect of eight or nine DMSO molecules as compared to three bidentate nitrate ions with a small bite and three or four DMSO molecules. Moreover, the average CN's of praseodymium, neodymium, and erbium perchlorates in nitromethane containing DMSO have been determined by IR measurements.[25] Reported data for $R = 20$ are 9.9, 9.3, and 8.7 for Pr, Nd, and Er, respectively, confirming the large variation in CN observed in the nitrate solutions. The other findings of this study are also in agreement with our conclusions regarding the variability of the coordination number with DMSO concentration and the small stability of the solvates with higher coordination numbers.

In conclusion, the systematic study presented in this communication clearly establishes what several partial studies were aiming to do, namely that coordination number changes occur along the lanthanide series and with the solvent composition. Both the position in the series and the magnitude of the changes depend upon the electronic and steric properties of the donors. A general trend of forming 9- and 8-coordinate solvates for lighter and heavier lanthanide ions, respectively, seems to prevail. However, solvates of low stability, with coordination numbers higher by one unit, can be easily obtained in the presence of an excess ligand, particularly when the latter is a strong donor. These findings shed new light on the interpretation of the irregularities often observed in the formation of lanthanide complexes.

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Supplementary Material Available: Tables of nitrate (Table T1) and bound MeCN (Table T2) vibrations in solutions of $Ln(NO_3)_3$ in acetonitrile and figures showing calibration curves for DMSO in acetonitrile (Figure F1) and absorbances of bound and free DMSO in solutions of $Ln(NO_3)_3$ in acetonitrile (Figure F2) (8 pages). Ordering information is given on any current masthead page.

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AM1 Parameters for Sulfur

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AM1 has been parametrized for sulfur. Calculations are reported for a wide range of sulfur-containing molecules. The calculated heats of formation and other properties of organosulfur molecules are much superior to those from MNDO and superior overall to those from PM3. AM1 calculations for several reactions agree well with experimental values. The results for compounds of sulfur in its higher valence states are also satisfactory, except for SF_4, where the error is probably due to the neglect of d AOs.

Introduction

Organosulfur chemistry has developed very rapidly in recent years[1] and now plays an integral role in organic chemistry. New types of structures found recently[2] in organosulfur compounds have enlarged our general knowledge of bonding and the electronic distributions in molecules. Many new reactions of compounds containing sulfur are now widely used in organic synthesis,[3] and many new types of biologically important organosulfur compounds have been discovered.[4]

The need for an effective theoretical treatment of organosulfur compounds is therefore clear. Use of ab initio procedures is restricted in this connection, as in many others,[5] by the computing time they need. Computational studies of chemical problems by adequate ab initio methods are frequently impracticable. These comments apply with special force to studies of chemical reactions, which require not only extensive exploration of potential surfaces but also the use of relatively high-level ab initio procedures, involving the use of split-plus-polarization basis sets and allowance for electron correlation. Sulfur presents more problems than the "organic" elements in this connection because it contains more orbitals and because the formal charge on it varies greatly, becoming very large in its higher valence states (S^{IV}, S^{VI}).

In organic chemistry, these difficulties have been largely solved by the development here of effective parametric ("semiempirical") procedures, in particular MNDO[6] and AM1,[7] which give results comparable[8] with those from quite good ab initio methods at less than one-thousandth of the cost. They are generally much superior to ones using minimum basis sets.[8] However, determined attempts to parametrize MNDO or AM1 for phosphorus or sulfur failed. No set of parameters could be found that gave satisfactory results for compounds containing them in all their valence states. In hindsight, this failure was due to one of the major problems met in developing semiempirical treatments such as AM1, i.e. the fact that the hypersurface representing the mean error as a function of the parameters (*parameter hypersurface*) usually has numerous minima and it is not easy to find the optimum one. While we would normally have continued the search for a better minimum, we were not unnaturally misled by the fact that split-plus-d basis sets have to be used in ab initio studies of compounds of P and S and the natural assumption that the same might be true in AM1. Recently, however, Dewar and Jie[9] succeeded in finding a better minimum on the parameter hypersurface for phosphorus, leading to a set of parameters that reproduced the properties of compounds containing it in both its valence states, and we have now likewise succeeded in finding a set of parameters that deals effectively with the even worse case of sulfur, where *three* valence states are involved. The effect of d AOs can apparently be largely compensated via the parametrization. However, as noted below, there are exceptional molecules where AM1 gives poor results and where the error can reasonably be attributed to d AOs, or changes in AOs, playing an unusually large role. A similar situation exists in the case of anions. In ab initio studies of anions, it is necessary to use a basis set containing diffuse AOs to allow for the orbital expansion due to negative charge. Yet, AM1 gives good results

Table I. Optimized AM1 Parameters for Sulfur

optimized params	AM1	MNDO	PM3
U_{ss}/eV	−56.694 056	−72.242 281	−49.895 371
U_{pp}/eV	−48.717 049	−56.973 207	−44.392 583
Z_s/au	2.366 515	2.312 962	1.891 185
Z_p/au	1.667 263	2.009 146	1.658 972
β_s/eV	−3.920 566	−10.761 610	−8.827 465
β_p/eV	−7.905 278	−10.108 433	−8.091 415
α/Å^{-1}	2.461 648	2.478 026	2.269 706
G_{ss}	11.786 329	12.880 000	8.864 667
G_{pp}	10.039 308	9.900 000	9.968 164
G_{sp}	8.663 127	11.260 000	6.785 936
G_{p2}	7.781 688	8.830 000	7.970 247
H_{sp}	2.532 137	2.260 000	4.041 836
K_1	−0.509 195		−0.399 191
K_2	−0.011 863		−0.054 899
K_3	0.012 334		
L_1	4.593 691		6.000 669
L_2	5.865 731		6.001 845
L_3	13.557 336		
M_1	0.770 665		0.962 123
M_2	1.503 313		1.579 944
M_3	2.009 173		

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