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FT IR and Fluorometric Investigation of Rare-Earth and Metallic Ion Solvation. 2. Europium Perchlorate and Nitrate in Anhydrous Solutions Containing Dimethyl Sulfoxide[1]

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The composition of the species in equilibrium in dilute and anhydrous solutions of $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ in acetonitrile containing Me_2SO and in Me_2SO itself is investigated by means of FT IR, fluorometric, and conductometric measurements. The data point to an absence of inner-sphere interaction between ClO_4^- and Eu^{3+} in solutions of $Eu(ClO_4)_3$ in Me_2SO. The composition of the solvate is determined by a quantitative study of the S–O and C–S stretching modes and of the emission spectra. When Me_2SO is added to anhydrous solutions of $Eu(ClO_4)_3$ 0.05 M in CH_3CN, solvent molecules are first expelled from the inner solvation sphere up to $R = [Me_2SO]_t/[Eu^{3+}]_t = 2$; then both solvent molecules and perchlorate ions are replaced. Equilibria occur between species containing seven, eight, and nine Me_2SO molecules. For $R \geq 12$, the average coordination number is $N = 8.7 \pm 0.5$, that is, a nonacoordinate species form, the symmetry of which may be close to a trigonal symmetry. A similar study of anhydrous $Eu(NO_3)_3$ solutions in CH_3CN indicates the formation of the nonacoordinate species $Eu(NO_3)_3(Me_2SO)_3$ ($N = 8.9 \pm 0.2$) for $R \geq 5$. For $R \geq 9$, nitrate ions start to dissociate: high-resolution spectra of the ${}^5D_0 \rightarrow {}^7F_0$ transition show the successive formation of $[Eu(NO_3)_n(Me_2SO)_x]^{(3-n)+}$, with n = 3, 2, 1, or 0. The average number of coordinated nitrate ions per Eu^{3+} ion, R_N, has been determined by two methods: IR absorbances at 818 and 832 cm^{-1} and intensity of the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition. $R_N = 0.4$ for $Eu(NO_3)_3$ solutions 0.05 M in Me_2SO. The apparent formation constant of the mononitrato species $[Eu(NO_3)(Me_2SO)_y]^{2+}$ amounts to 1.1 ± 0.2 M^{-1}. The $Eu-O(Me_2SO)$ vibration absorbs at 186 cm^{-1}. The fluorescence lifetimes of 0.1 M solutions in Me_2SO are equal to 1.57 and 1.35 ms for $Eu(ClO_4)_3$ and $Eu(NO_3)_3$, respectively. The quantum yield of the nitrate solution is 20.4%.

Introduction

FT IR is a useful tool for the study of coordinated ions in solution. The high photometric accuracy of this technique allows a precise determination of the number of both neutral and ionic ligands bonded in the first coordination sphere of a metallic ion. In the first part of this series,[2] we have shown how FT IR difference spectra can be used along with fluorescence data to investigate the solvation of the europium ion in anhydrous and dilute (0.05 M) solutions of $Eu(ClO_4)_3$ in acetonitrile. The experimental data were consistent with the presence of two main nonacoordinated species in equilibrium: $[(EuClO_4(m))(CH_3CN)_8]^{2+}$ (~60%) and $[Eu(CH_3CN)_9]^{3+}(ClO_4(b))^-$ (~30%), where m and b stand for mono- and bidentate, respectively. An average coordination number of N of 9.1 ± 0.3 was found for the Eu^{3+} ion.

In this paper we report a similar study of anhydrous solutions containing a strongly coordinating ligand, dimethyl sulfoxide (Me_2SO). IR and emission data on both $Eu(ClO_4)_3/Me_2SO/CH_3CN$ and $Eu(NO_3)_3/Me_2SO/CH_3CN$ systems are presented and analyzed.

Experimental Section

Anhydrous europium perchlorate[2] and nitrate[3] and acetonitrile[2] were prepared as previously described. Dimethyl sulfoxide of spectroscopic quality (Fluka) was used without additional purification. All the solutions were prepared and stored under a strictly controlled atmosphere (N_2 with less than 5 ppm of H_2O). The emission spectra and lifetimes were measured as previously reported.[4,5] FT IR difference spectra were recorded with a Bruker IFS-113c interferometer[2] using the following conditions: far-IR 8-cm^{-1} resolution, 500 scans, polyethylene windows, 30-μm path length; middle-IR 1-cm^{-1} resolution, 256 scans, AgCl windows, 23–25-μm path length. For quantitative data, at least two independently prepared solutions were measured.

Table I. Emission Spectra of Anhydrous Solutions of $Eu(ClO_4)_3$ 0.2 M in Me_2SO[a]

		${}^7F_0$	${}^7F_1$	${}^7F_2$	${}^7F_3$	${}^7F_4$	${}^7F_5$
${}^5D_0$	λ	579.5	591.5	612.5	651	692	746.5
			593.5	614.3	653	699.5	753
				616.1	654.5		
				618.8	659		
	I	0.26	100	140	9	150	1
${}^5D_1$	λ	527	536.5	553.5	585	627.5	
			538	557.8			
				559.5			
	I	0.5	3	4	b	b	

[a] λ is in nm; I represents the relative integrated and corrected area of the emission bands. [b] Not determined; these transitions appear as shoulders of transitions from the ${}^5D_0$ level.

Other experimental details are described elsewhere.[4]

Results and Discussion

Europium Perchlorate. The molar conductivities of 0.001 and 0.01 M solutions of $Eu(ClO_4)_3$ in Me_2SO are 125 and 78 Ω^{-1} mol^{-1} cm^2 at 25 °C, respectively. The former value is clearly in the accepted range for 3:1 electrolytes[6,7] whereas the latter indicates that some interaction takes place between the europium and the perchlorate ions. The emission spectra, which are sensitive to inner-sphere interaction,[8] of 0.05 and 0.2 M solutions are identical: both the energies of the transitions from the excited ${}^5D_0$ and ${}^5D_1$ levels and their relative intensities are the same (Figure 1, Table I), as well as the fluorescence lifetimes, 1.57 ms. This points to an absence of inner-sphere interaction between Eu^{3+} and ClO_4^-, and the solvated species can therefore be formulated as $[Eu(Me_2SO)_n]^{3+}$. To investigate the solvation of the Eu^{3+} ion in the presence of Me_2SO, we have measured the spectroscopic

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(1) Abstracted, in part, from the Ph.D. theses of C.M. and J.-R.Y.

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

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

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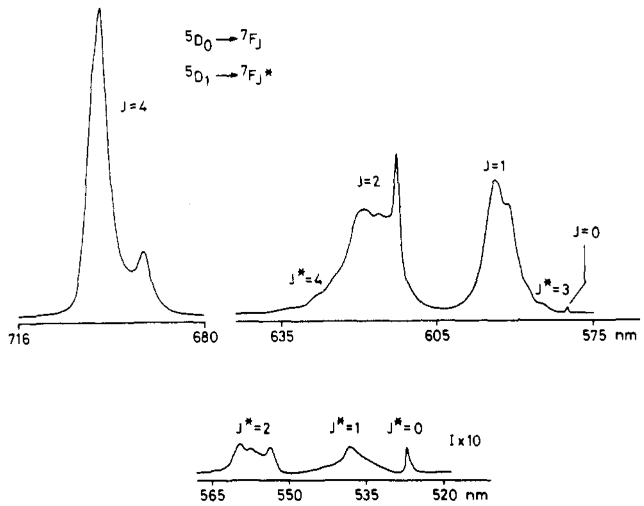

Figure 1. Part of the emission spectrum of an anhydrous solution of $Eu(ClO_4)_3$ 0.05 M in Me_2SO: excitation to the $^5L_6$ level 394 nm; analyzing band-pass 0.2 nm; vertical scale in arbitrary units. The scale of the bottom spectrum is magnified 10 times.

Table II. Vibrations of Bulk and Coordinated Me_2SO ($\bar{\nu}_{max}$ in cm^{-1}, 300-1500 cm^{-1}) for $Eu(ClO_4)_3$ Solutions 0.05 M in Anhydrous Acetonitrile Containing Various Concentrations of Me_2SO

assignt[13]	bulk Me_2SO	coordinated Me_2SO	Δ^a
ν_{12} (A′)	304 sh	314	10
ν_{23} (A″)	335	350	15
ν_{11} (A′)	380	413	33
ν_{10} (A′)	669	680	11
ν_{22} (A″)	696.5-698	715-719.5	17-18.5
ν_9 (A″)	890-894	902-905	11-12
	927-930	942-943	13-15
ν_{21} (A′)	952	961-965	9-13
ν_{20} (A′)	*b*	$(1015)^b$	
ν_7 (A′)	1060-1062	1003-1009	−51 to −53
ν_6	1293-1294	1298-1302	4-7
	1310-1311	1318-1323	9
ν_{19}	1332-1334	*c*	
ν_5 (A″)	1405-1407	*c*	
ν_4	1416-1420	*c*	
ν_{18} (A′)	1438-1442	*c*	

[a] $\bar{\nu}$(coord) − $\bar{\nu}$(bulk); observed when both species are simultaneously present. [b] Masked by ν_7(coord). [c] Not observed.

properties of anhydrous $Eu(ClO_4)_3$ solutions in CH_3CN containing various amounts of Me_2SO.

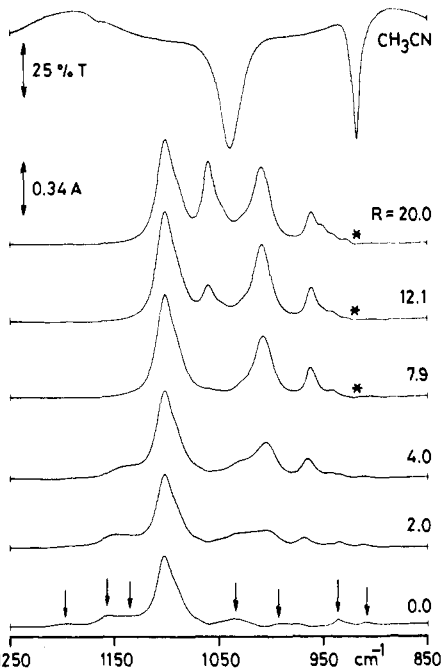

Figure 2. FT IR difference spectra (850-1250 cm^{-1}, absorbance units) of anhydrous $Eu(ClO_4)_3$ 0.05 M in CH_3CN in the presence of Me_2SO, along with the transmission spectrum of the solvent. $R = [Me_2SO]_t/[Eu^{3+}]_t$. Stars denote artifacts due to incomplete solvent compensation. Arrows point to absorption bands due to mono- and bidentate perchlorate ions.

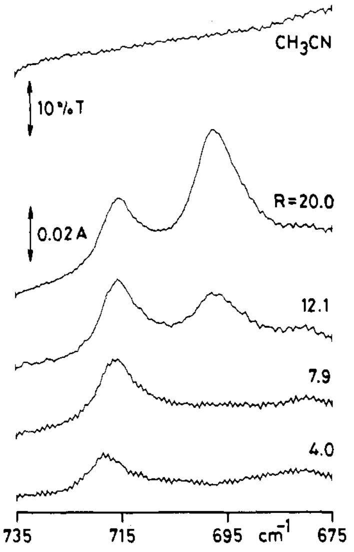

Figure 3. FT IR difference spectra (675-735 cm^{-1}, absorbance units) of anhydrous $Eu(ClO_4)_3$ 0.05 M in CH_3CN in the presence of Me_2SO ($R = [Me_2SO]_t/[Eu^{3+}]_t$), along with the transmission spectrum of the solvent. The modulation of the spectrum arises from multiple reflections on the windows of the MCT detector.

The emission spectra and lifetimes show drastic changes with $R = [Me_2SO]_t/[Eu^{3+}]_t$ that may be summarized as follows (Table S1, supplementary material). (i) The relative intensity of the forbidden $^5D_0 \rightarrow {}^7F_0$ transition, with respect to the intensity of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$,[9] increases sharply from 1% ($R = 0$) to 9% ($R = 2$) and then decreases to 2% ($R = 4$) and to 0.3% ($R = 20$). (ii) The relative intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition follows a similar trend: 1.7, 4.4, 3.2, and 1.6 for $R = 0$, 4, 6, and 20, respectively. (iii) The fluorescence lifetime decreases from 2.10 ms ($R = 0$) to 1.12 ms ($R = 4$) and increases again to 1.31 ($R = 6$) and 1.55 ms ($R = 20$). (iv) Most of the changes occur between $R = 0$ and $R = 10$, and the data for $R = 20$ are very close to those obtained in pure Me_2SO. Similar changes have been observed for other, hydrated, europium salts.[11] This reflects a rather complicated situation in which differently solvated species are successively formed from the initial ones.

We have turned to FT IR measurements to monitor the concentration changes of bonded and free Me_2SO, of ionic and mono- and bidentate perchlorate ions, and of coordinated CH_3CN molecules. A total of 16 solutions with R between 0 and 20 were investigated. Part of the spectra are displayed in Figures 2 and 3, and Me_2SO vibrations are listed in Table II.[12] Complexed Me_2SO molecules have IR absorptions that

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(9) This transition may be used as the internal standard for intensity comparison since it is not affected by the environment of the fluorescent ion.[10]

(10) Porcher, P.; Caro, P. *J. Lumin.* **1980**, *21*, 207.

(11) Chrysochoos, J.; Evers, A. *J. Lumin.* **1973**, *6*, 335.

(12) The energies of the vibrations of mono- and bidentate ClO_4^- and of coordinated CH_3CN are not much affected by the addition of Me_2SO. They were previously tabulated.[2]

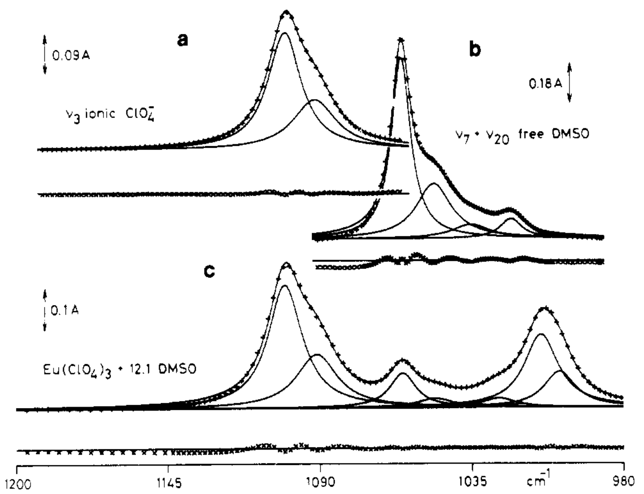

Figure 4. Deconvoluted spectra (solid lines) with Lorentzian functions: (a) ionic perchlorate, ν_3 (T_2), $Eu(ClO_4)_3$ 0.05 M in CH_3CN + 0.20 M NO_3^-; (b) bulk Me_2SO, $\nu_7 + \nu_{20}$, 1 M solution in CH_3CN; (c) $Eu(ClO_4)_3$ 0.05 M in CH_3CN + 0.6 M Me_2SO.

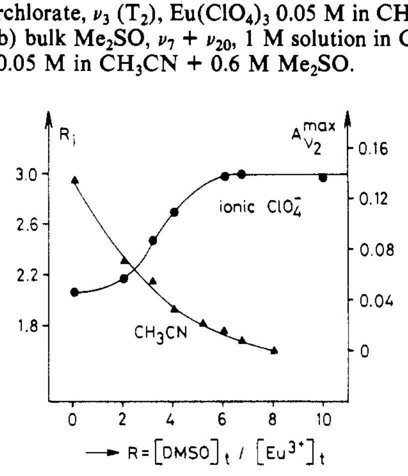

Figure 5. Number of ionic ClO_4^- groups per Eu^{3+} ion, R_i, and variation of A_{ν_2}(max) (2283 cm^{-1}) of coordinated CH_3CN molecules vs. the ratio $R = [Me_2SO]_t/[Eu^{3+}]_t$, $Eu(ClO_4)_3$ solutions 0.05 M in CH_3CN/Me_2SO.

are shifted; the largest shifts occur for the S–O stretch (ν_7) and for the asymmetric C–S stretch (ν_{22}). The latter vibration is free from interferences, but its molar absorption coefficient is small, whereas the stronger absorptions corresponding to ν_7 arise in a spectral range in which the perchlorates also absorb. Moreover, ν_7 appears as a composite band containing 2–3 components. To minimize errors, we have used both vibrations for quantitative determinations, and the spectra of the solutions with $R > 7$ were deconvoluted with use of Lorentzian band shapes (Table S2 (supplementary material), Figure 4).

When increasing amounts of Me_2SO are added to the perchlorate solutions, acetonitrile molecules are displaced first out of the inner coordination sphere (Figure 5): the number of ionic ClO_4^- groups per Eu^{3+} ion, R_i, remains almost constant up to $R = 2$ and then increases sharply to reach 3.0 for $R > 10$. Far-IR spectra also illustrate this point: a broad band at 217 cm^{-1}, corresponding to the $Eu-O(ClO_4^-)$ vibration, is still present when $R = 4$, and the $Eu-O(Me_2SO)$ vibration absorbs at 186 cm^{-1}. Also, the bands corresponding to ClO_4^-(b) disappear first ($R > 4$); this confirms that the ClO_4^-(m) groups are in the inner coordination sphere. Me_2SO molecules are quantitatively coordinated up to a ratio $R = 7.7 \pm 0.1$, as shown by the absence of absorption bands of free

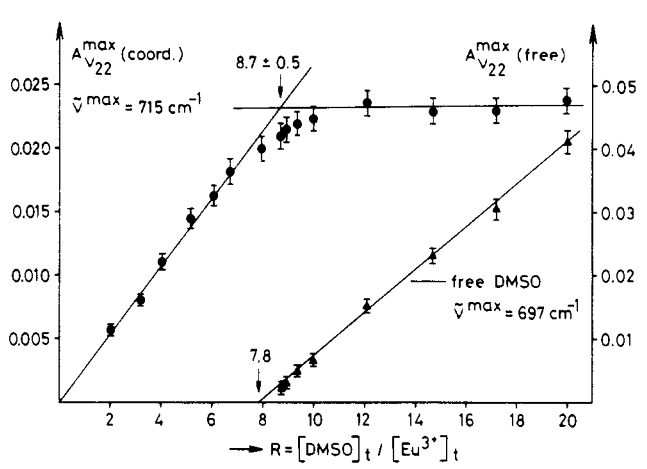

Figure 6. Absorbances of the ν_{22} vibrations of bulk and coordinated Me_2SO, $Eu(NO_3)_3$ 0.05 M in CH_3CN/Me_2SO ($R = [Me_2SO]_t/[Eu^{3+}]_t$).

Me_2SO (Figure 6). Equilibria then occur between species containing different numbers of coordinated Me_2SO molecules, n = 7, 8, and 9. The concentration of coordinated Me_2SO reaches a plateau for $R > 12$, and it corresponds to the presence of one main, nonacoordinated species: the intersections of the limiting straight lines for both ν_{22} (Figure 6) and ν_7 yield an average number of coordinated Me_2SO molecules per Eu^{3+} ion of 8.7 ± 0.5. Since no other ligand is bonded to the metal ion, this number represents the average coordination number of Eu^{3+} in such solutions. Our data are not accurate enough to determine the position of the equilibria

$$[Eu(Me_2SO)_{n-1}]^{3+} + Me_2SO \rightleftarrows [Eu(Me_2SO)_n]^{3+}$$

For $n = 9$, however, the apparent equilibrium constant may be estimated to be $\sim$10 M^{-1}, so that in pure Me_2SO the nonacoordinate species will be largely predominant. The intensities of the transitions from the $^5D_0$ level, $^7F_0/^7F_1$, $^7F_2/^7F_1$, and $^7F_4/^7F_1$, are equal to 0.003, 1.5, and 1.9, respectively. The last two values are representative of a species without an inversion center. The small number of observed crystal field components for the $J = 1$ and $J = 4$ levels points, however, to an arrangement of the oxygen atoms around the metal ion which could be close to a coordination polyhedron possessing a trigonal symmetry. Some features of the MCD spectra of anhydrous solutions of $EuCl_3$ in Me_2SO have recently been discussed in terms of D_{3h} and C_{3h} symmetries.[14]

Adducts of formula $Ln(ClO_4)_3 \cdot nMe_2SO$ have been isolated with $n = 8$ (La–Tb) and $n = 7$ (Dy–Lu).[15,16] Arguments based on the comparison of the absorption spectra of $Nd(ClO_4)_3 \cdot 8Me_2SO$ and of $Nd(ClO_4)_3 \cdot 6H_2O$ solutions in Me_2SO[16] on one hand and on the energies of the absorption bands of $Ln(ClO_4)_3 \cdot 6H_2O$ solutions in CH_3NO_2/Me_2SO (Ln = Pr, Nd, Er)[17] on the other hand have led some authors to postulate that in solution not all the Me_2SO molecules are coordinated in the inner solvation sphere. Our data do not support this conclusion for the following reasons. (i) Difference IR spectra of solutions with different R's do not show the presence of differently coordinated Me_2SO molecules. (ii) High-resolution (0.01-nm) excitation spectra have been recorded for the solid adduct $Eu(ClO_4)_3 \cdot 7.5Me_2SO$[18] and for

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(13) Horrocks, W. D., Jr.; Cotton, F. A. *Spectrochim. Acta* **1961**, *17*, 134. Forel, M. T.; Tranquille, M. *Spectrochim. Acta, Part A* **1970**, *26A*, 1023.

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(15) Krishnamurthy, V. N.; Soundararajan, S. *J. Inorg. Nucl. Chem.* **1967**, *29*, 517. Iwase, A.; Tada, S. *Nippon Kagaku Kaishi* **1973**, 60.

(16) Lugina, L. N.; Davidenko, N. K. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1322.

(17) Lugina, L. N.; Davidenko, N. K.; Yatsimirskii, K. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1973**, *18*, 1453.

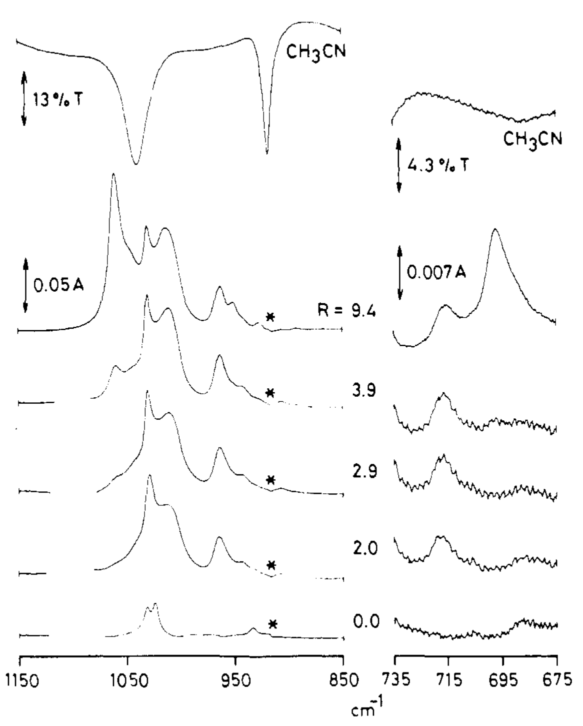

Figure 7. Parts of the FT IR difference spectra (absorbance units) of $Eu(NO_3)_3$ 0.05 M in CH_3CN/Me_2SO ($R = [Me_2SO]_t/[Eu^{3+}]_t$), along with the transmission spectrum of the solvent. Stars denote artifacts due to incomplete solvent compensation.

solutions having $R = 2.7$, 7.4, and 18.3. The $^5D_0 \leftarrow {}^7F_0$ transition has two components for the former, at 579.7 and 579.9 nm; they correspond to species with $n = 7$ and 8. Only one component is observed for the solutions, the maximum of which is regularly shifted: 579.2 ($R = 2.7$, fwhh = 0.9 nm, asymmetric peak), 579.3 ($R = 7.4$, fwhh = 0.8, asymmetric peak), and 579.4 nm ($R = 18.3$, fwhh = 0.5, symmetric peak). (iii) The other fluorescence data, relative intensities and lifetimes (Table S1), undergo changes of 10–20% between $R = 9$ and $R = 20$, which are difficult to account for by an outer-sphere interaction only.

Finally, we would like to mention that the average coordination number N we have found is in agreement with similar determinations for $Ln(ClO_4)_3 \cdot 6H_2O$ in CH_3NO_2/Me_2SO: $N = 9.9$, 9.3, and 8.7 for Ln = Pr, Nd, and Er, respectively, and for $R = 20$.

Europium Nitrate. When Me_2SO is added to anhydrous solutions of $Eu(NO_3)_3$ in CH_3CN, it quantitatively displaces the bonded CH_3CN molecules, as illustrated by the FT IR spectra partly displayed in Figure 7. The nitrate absorptions occur at 740, 818, 1029, 1309, and 1493 cm^{-1}. The broad bands centered at 235 (with a shoulder at 216 cm^{-1}), 220, and 216 cm^{-1} for solutions with $R = [Me_2SO]_t/[Eu^{3+}]_t = 0$, 2, and 6, respectively, are assigned to $Eu-O(NO_3)$ vibrations. The $Eu-O(Me_2SO)$ vibration absorbs at the same wavenumber as for the perchlorate solutions (186 cm^{-1}), and so do all the Me_2SO vibrations; the only difference is a slightly smaller shift for ν_7 upon complexation, -47 to -50 cm^{-1}. Quantitative determinations using the ν_7 and ν_{22} bands indicate the presence of free Me_2SO molecules when $R > 2.3 \pm 0.2$ and lead to an average number of coordinated sulfoxide molecules of 2.9 ± 0.2. We have therefore again the formation of a nonacoordinate species,[19] which, for $2 < R < 4$, is in equilibrium with another species.

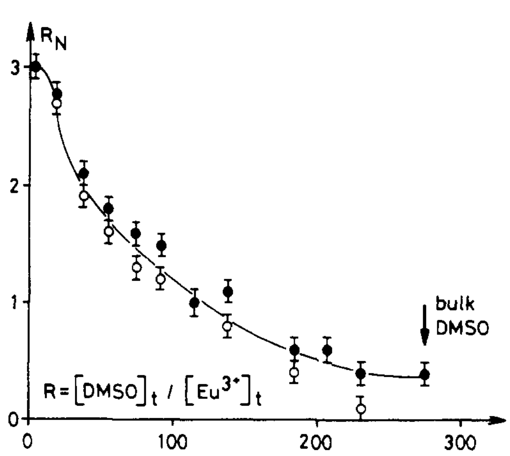

Figure 8. Average number of coordinated NO_3^- ions per Eu^{3+} ion vs. the ratio $R = [Me_2SO]_t/[Eu^{3+}]_t$, $Eu(NO_3)_3$ 0.05 M in CH_3CN/Me_2SO: (●) estimated from IR data; (○) estimated from fluorescence data.

The structural and spectroscopic properties of the solid adducts $Ln(NO_3)_3 \cdot nMe_2SO$ have been extensively studied;[20] lighter lanthanoid ions are 10-coordinate (La–Gd, $n = 4$) whereas heavier ions are 9-coordinate (Tb–Lu, $n = 3$). When dissolved in CH_3CN, the europium adduct clearly dissociates into the nonacoordinate species $Eu(NO_3)_3(Me_2SO)_3$ as shown by the presence of IR absorptions from free Me_2SO molecules and by the absence of bonded CH_3CN molecules. When the europium nitrate is compared to the europium perchlorate, for which a higher coordination number is observed in solution than in the solid state (9 vs. 8), we have a reverse situation (9 vs. 10). This may be explained by a weaker interaction, reflected by the smaller ν_7 shift upon complexation, between Me_2SO and the neutral $Eu(NO_3)_3$ molecule, as compared to the interaction between Me_2SO and the Eu^{3+} ion in $Eu(Me_2SO)_9^{3+}$.

The emission spectra (Table S3, supplementary material) indicate that the nitrate ions begin to dissociate when $R > 9$: the $^5D_0 \rightarrow {}^7F_0$ transition, at 580.25 nm, assigned to $Eu(NO_3)_3(Me_2SO)_3$, possesses a weak shoulder at 580.0 nm, the intensity of which increases when more Me_2SO is added. This latter component, assigned to $[Eu(NO_3)_2(Me_2SO)_x]^+$, is predominant when $R > 37$. Upon addition of larger amounts of Me_2SO, other components appear at 579.85 nm ($R > 92$, $[Eu(NO_3)(Me_2SO)_y]^{2+}$) and 579.45 ($R > 200$, $[Eu(Me_2SO)_n]^{3+}$). We have estimated the average number of coordinated nitrate ions per Eu^{3+} ion, R_N, by use of two independent methods.

The first one takes advantage of the weak IR absorptions of the ionic and bonded (bidentate) nitrates at 832 and 818 cm^{-1}, respectively. The second one implies the intensity of the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$; indeed, for $Eu(ClO_4)_3$ solutions containing nitrate ions and Me_2SO molecules in such concentrations that the inner coordination sphere of the europium ion is only comprised of these two species, the intensity of this transition increases linearly with the number of coordinated nitrates. The results are presented in Figure 8; they are in very good agreement up to $R = 180$. Above this ratio, outer-sphere interactions make fluorescence data less reliable than IR data. These results indicate that $Eu(NO_3)_3$ solutions 0.05 M in Me_2SO contain two species in equilibrium, [Eu-

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(18) Treatment of $Eu(ClO_4)_3 \cdot 8Me_2SO$ under vacuum leads to the progressive loss of one molecule of Me_2SO.

(19) Raman polarization measurements indicate that nitrate ions are bidentate ligands in CH_3CN: Bünzli, J.-C. G.; Yersin, J.-R.; Mabillard, C., unpublished results.

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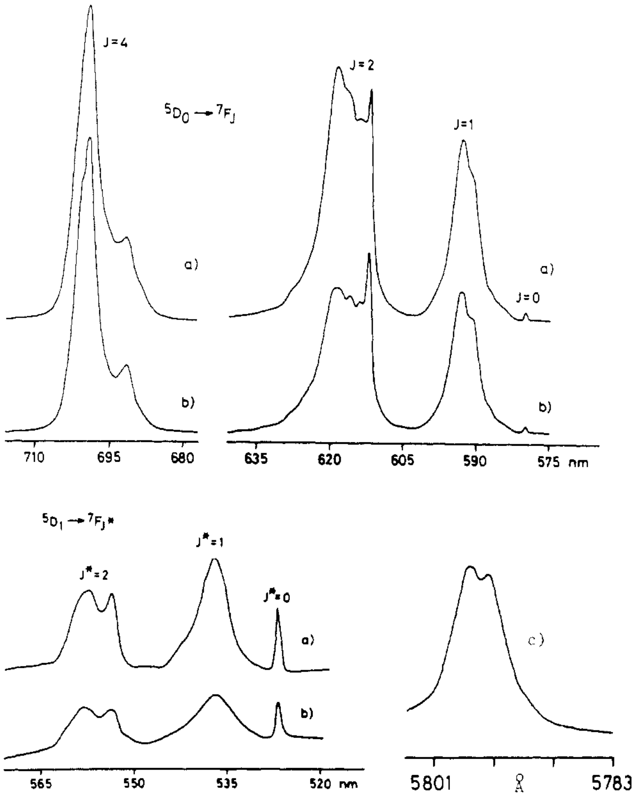

Figure 9. Emission spectra of anhydrous Me_2SO solutions with $Eu(NO_3)_3$ of the following concentrations (λ_{exc} = 394 nm): (a) 0.1 M; (b) 0.01 M; (c) 0.1 M, $^5D_0 \rightarrow {}^7F_0$ transition.

$(NO_3)(Me_2SO)_y]^{2+}$ and $[Eu(Me_2SO)_n]^{3+}$, in the approximate ratio 1:6.5. The number of coordinated Me_2SO molecules could not be determined with sufficient accuracy from IR data.[21] However, if we refer to the above discussion, n is likely to be equal to 9 and y to 7.

The inner-sphere interaction of the nitrate ion is further evidenced by conductivity and fluorescence data (Figure 9). The molar conductivities of $Eu(NO_3)_3$ solutions 10^{-4}, 5×10^{-4}, 10^{-3}, 2×10^{-3}, and 4×10^{-3} M in Me_2SO are equal to 115, 107, 102, 101, and 73 Ω^{-1} mol^{-1} cm^2, respectively, at 25 °C. These values are slightly smaller than the conductivities found for the perchlorate solutions. The emission spectrum of a 0.01 M solution (lifetime 1.40 ms) is similar to the spectra of the perchlorate solutions, whereas the spectrum of 0.1 M $Eu(NO_3)_3$ (lifetime 1.35 ms) displays substantial intensity changes (Figure 9). The $^5D_0 \rightarrow {}^7F_0$ transition is comprised of two components, at 579.55 and 579.15 nm, corresponding to the two above-mentioned solvated species. It is interesting to note its large intensity variation when Me_2SO molecules are removed from the first coordination sphere of the Eu^{3+} ion. For solutions 0.05 M in Eu^{3+}, $^7F_0/^7F_1$ amounts to 0.3, 0.9, 1.2, 1.4, and 10% for $[Eu(Me_2SO)_9]^{3+}$, $[Eu(NO_3)(Me_2SO)_y]^{2+}$, $[Eu(NO_3)_2(Me_2SO)_x]^+$, $Eu(NO_3)_3(Me_2SO)_3$, and $Eu(NO_3)_3(CH_3CN)_3$, respectively.

The quantum yield of the $^5D_0$ emission upon excitation to the $^5L_6$ level for $Eu(NO_3)_3$ 0.1 M in Me_2SO amounts to 20.4%, as measured by taking $Eu(NO_3)_3 \cdot 6H_2O$ 0.1 M in CH_3OH as standard (Q = 5%[22]).

The apparent equilibrium ratio $[Eu(NO_3)(Me_2SO)_7{}^{2+}]$:$[Eu(Me_2SO)_9{}^{3+}] \cdot [NO_3{}^-]$ can be estimated to 1.1 ± 0.2 M^{-1} for a $Eu(NO_3)_3$ solution 0.05 M in Me_2SO. The corresponding value we have reported for aqueous solutions was 0.3 ± 0.1 M^{-1}. With the assumption that each nitrate displaces two solvent molecules, these ratios have to be multiplied by the square of the solvent concentrations, $[S]^2$, to obtain the apparent constants, K_{app}, of the equilibria

$$[EuS_n]^{3+} + NO_3^- \rightleftarrows [Eu(NO_3)S_{n-2}]^{2+} + 2S$$

The K_{app} values are approximately equal to 200 and 900 M for Me_2SO and H_2O, respectively, which reflects the stronger affinity of the europium ion for the dimethyl sulfoxide molecules.

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Registry No. Eu, 7440-53-1; Me_2SO, 67-68-5; $Eu(NO_3)_3$, 10138-01-9; $Eu(ClO_4)_3$, 13537-22-9.

Supplementary Material Available: Listings of emission intensities and lifetimes of 0.05 M $Eu(ClO_4)_3 \cdot R(Me_2SO)$ in CH_3CN ($0 \leq R \leq 20.3$) (Table S1), deconvolutions of IR spectra of the above-mentioned solutions (1000–1100 cm^{-1}) (Table S2), and emission intensities and lifetimes of 0.05 M $Eu(NO_3)_3 \cdot R(Me_2SO)$ in CH_3CN ($4 \leq R \leq 275$) (Table S3) (3 pages). Ordering information is given on any current masthead page.

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[21] The numbers of y and z could not be accurately determined from the IR data because of the presence of large absorptions arising from bulk Me_2SO molecules.

[22] Dawson, W. R.; Kropp, J. L. *J. Opt. Soc. Am.* **1965**, *55*, 822.

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Magnetic and Mössbauer Resonance Investigations of the Weak Ferrimagnet $Fe_2(MoO_4)_3$

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Magnetic and Mössbauer resonance measurements have shown that $Fe_2(MoO_4)_3$ exhibits below an ordering temperature of about 13 K a weak ferrimagnetism due to incomplete compensation of the magnetization of antiferromagnetically coupled sublattices. From the analysis of the exchange links Fe–O–Mo–O–Fe and from the Mössbauer resonance spectra a possible arrangement of the spins has been deduced.

Introduction

The catalytic properties of $Fe_2(MoO_4)_3$ are well-known in the process of selective oxidation of methanol to formaldehyde. Ferric molybdate is also present in multicomponent catalysts used for the ammoxidation of propene to acrylonitrile and for the oxidation of propene to acrolein.

Numerous studies have been carried out in order to try to improve the activity of these catalysts.[1-8] However, the few