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Spectroscopic Analysis of the Complexes of the Eu^{3+} Ion with 1-Hydroxyethane-1,1-diphosphonic Acid in the Solid State and in a 2 M $NaNO_3$ Solution

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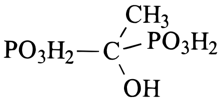
The absorption and luminescence spectra of the solid compound $Eu\{[C(CH_3)(OH)(PO_3H_2)(PO_3H)][C(CH_3)(OH)(PO_3H)_2]\}$ (also written as $Eu(H_3L)(H_2L)$) are measured by dispersing the microcrystalline complex in a silicone film. Nine free ion levels and eight crystal field levels are identified. A set of 20 free ion parameters for Eu^{3+} is optimized. The crystal field levels are calculated using these optimized free ion levels combined with a set of crystal field parameters for the analogous Er^{3+} complex assuming a C_{2v} site symmetry. The experimental crystal field levels are in good agreement with the calculated levels. This means that the site symmetry of both lanthanide ions in this complex can be described by a C_{2v} point symmetry. In acidic (pH < 2) solutions in 2 M $NaNO_3$ medium, Eu^{3+} and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) form several complexes. By measuring the overall absorption spectra of Eu^{3+} and HEDP as function of the ratio Eu^{3+}/HEDP and at different pH values, the absorption spectra of the $Eu(H_3L)^{2+}$, $Eu(H_3L)_2{}^+$, and $Eu(H_3L)_2(H_2L)^-$ complexes are deduced. By analysis of the shape of the hypersensitive transition, $^5D_2 \leftarrow {}^7F_0$, and the intensities of all the electric dipole transitions of the Eu^{3+} ion, it was found that the site symmetry of the Eu^{3+} ion in the $Eu(H_3L)_2(H_2L)^-$ complex is similar to the site symmetry of the Eu^{3+} in the neutral $Eu(H_3L)(H_2L)$ solid complex. The site symmetry of the Eu^{3+} ion in the $Eu(H_3L)^{2+}$ and in the $Eu(H_3L)_2{}^+$ complexes was found to be similar to the site symmetry of the free Eu^{3+} in 2 M $NaNO_3$ solution.

1. Introduction

1-Hydroxyethane-1,1-diphosphonic acid (HEDP) is a tetraprotic acid (H_4L) that forms protonated coordination complexes with several metal cations.[1] The complexes are stable in solutions of acidities greater than pH 2.[2] A structural formula of the acid is shown in Figure 1 for clarity.



$$PO_3H_2-\overset{CH_3}{\underset{OH}{C}}-PO_3H_2$$

Figure 1. Structural formula for HEDP.

This paper reports a spectroscopic analysis of the solid complex, $Eu(H_3L)(H_2L)$, as well as of different ionic complexes of Eu^{3+} and HEDP in solution. A set of free ion parameters for the Eu^{3+} ion is optimized by least-squares fitting to the experimental free ion levels. The site symmetry is deduced with the help of the crystal field parameters of the analogous Er^{3+} complex.[3] This is necessary because the number of experimental crystal field levels that can be determined in the absorption spectrum of the $Eu(H_3L)(H_2L)$ complex is too small for the quantitative analysis.[4]

The complexes of Eu^{3+} and HEDP formed in a 2 M $NaNO_2$ solution are reported in the second part of the paper. The spectra of individual complexes are obtained from the overall absorption spectra of solutions containing different ratios of Eu^{3+}/HEDP using a systematic complexation procedure by pH control. The absorption spectra of these complexes are compared to the absorption spectrum of the solid $Eu(H_3L)(H_2L)$ complex in order to investigate the site symmetry of the complexes in solution.

2. Experimental Section

2.1. Preparation of the Crystalline $Eu(H_3L)(H_2L)$ Complex. Crystals of $Eu\{[C(CH_3)(OH)(PO_3H_2)(PO_3H)][C(CH_3)(OH)(PO_3H)_2]\}$ are obtained at room temperature by dissolution of Eu_2O_3 in a 30% aqueous solution of HEDP (molar ratio HEDP/Eu_2O_3 = 4). Slow evaporation at room temperature results in the formation of very tiny needlelike colorless crystals. The similarity of these crystals and crystals of similar compounds with other lanthanides[3] is to be pointed out here. R. Rochdaoui already demonstrated the isomorphous behavior of the lanthanides in these complexes using vibrational Raman and vibrational infrared spectroscopy.[5]

2.2. Preparation of the Stock Solutions. Stock solutions of HEDP (0.4−0.7 M) are prepared by dissolving anhydrous HEDP (Fluka, 99.99% pure reagent) into deionized water. The concentrations are determined by potentiometric titration with a standard NaOH solution. The carbon dioxide in the stock solution is excluded by bubbling N_2 gas through the solution before and during the titration.

A 0.1 M stock solution of Eu^{3+} is prepared by dissolving Eu_2O_3 (Acros, 99.99% pure reagent) in a 0.3 M HNO_3 solution. The Eu^{3+} concentration of this solution is determined by the method of Flashka.[6,7]

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(3) Martello, P.; Görller-Walrand, C.; D'Olieslager, W.; Silvestre, J.-P.; Rochdaoui, R.; Lee, M.-R.; Nguyen Quy Dao *Inorg. Chem.* To be submitted.

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(5) Rochdaoui, R. Ph.D. Thesis, Ecole Centrale, Paris, 1991.

S0020-1669(97)01624-8 CCC: $15.00

2.3. Preparation of the Solutions. To obtain measurable spectroscopic signals of the $^5D_J \leftarrow {}^7F_0$ transitions, accurately measured volumes of both stock solutions are diluted with deionized water and the necessary amount of $NaNO_3$ in a volumetric flask so that an Eu^{3+} concentration of at least 0.02 mol L^{-1} is realized.

2.4. Spectroscopic Measurements. Since the $Eu(H_3L)(H_2L)$ complex could not be prepared as monocrystals, the solid microscopic needles are crushed and the powder is mixed with silicone grease. A transparent film of this mixture is brought between two quartz glasses. UV−visible absorption spectra are taken with an AVIV 17DS spectrophotometer at liquid helium temperature (4.2 K), nitrogen temperature (77 K), and finally at room temperature for comparison with the spectra of Eu^{3+}/HEDP complexes in solution. The resolution of this instrument is 0.1 nm in the UV region and 0.3 nm in the near-infrared region. Luminescence spectra are recorded with a SPEX Fluorolog 1691 spectrofluorimeter using a spectral bandwidth of 0.36 nm for both excitation and emission slit. UV−visible absorption spectra of the solutions in a 10 cm cell are obtained using an AVIV 17DS spectrophotometer at room temperature.

3. Spectroscopic Analysis of the $Eu(H_3L)(H_2L)$ Complex

3.1. Simulation of the Energy Level Scheme. The $^{2S+1}L_J$ states of Eu^{3+} were calculated as a function of a set of 20 free ion parameters. The Hamiltonian, H, defined by Crosswhite et al.,[8] can be expanded as in eq 1:

$$H = E_{AVG} + \sum_k F^k f_k + \zeta_{nl} A_{SO} + \alpha L(L+1) + \beta G(G_2) + \gamma G(G_7) + \sum_i T^i t_i + \sum_k P^k p_k + \sum_k M^k m_k \quad (1)$$

The Hamiltonian contains a set of repulsion parameters (F_2, F_4, F_6), the spin−orbit coupling parameter (ζ_{nl}), two-body configuration interaction parameters (α, β, γ), three-body configuration interaction parameters (T^2, T^3, T^4, T^6, T^7, T^8), and the magnetic interaction parameters (P^2, P^4, P^6, M^0, M^2, M^4). The E_{AVG} parameter represents the spherically symmetric part of the perturbation. With this energy operator, H, a matrix is constructed, the diagonalization of which results in free ion levels. The angular parts of the matrix elements (f_K, A_{SO}, ...) can be calculated exactly. The 20 parameters concern the radial parts, which cannot be calculated.

4. Spectroscopic Analysis of the Complexes in Solution

4.1. Systematic Complexation by pH Control. In 2 M $NaNO_3$ medium, Eu^{3+} and 1-hydroxyethane-1,1-diphosphonic acid form several complexes in acidic solutions (pH < 2).[2] The concentrations of these complexes change with the pH of the solution, the total Eu^{3+} concentration (C_{Eu}) and/or the total HEDP concentration (C_L). To calculate the concentrations of the different complexes present, the acidity constants of HEDP and the formation constants of the Eu^{3+}−HEDP complexes determined by K. L. Nash et al.[2] are used. At pH values lower than 2, five complexes are formed, namely, $Eu(H_3L)^{2+}$, $Eu(H_2L)^+$, $Eu(H_3L)_2{}^+$, $Eu(H_3L)(H_2L)$, and $Eu(H_3L)_2(H_2L)^-$.

The aim of the systematic complexation by pH control is the determination of the concentrations of the several complexes in solution. The concentrations of all the complexes in the solution can be calculated if C_{Eu}, C_L, and the pH of the solution are known. To calculate these concentrations, one has to solve the mass balance equation in the free HEDP concentration, $[L_\nu]$:

$$C_L + (\beta_{111}\alpha_2[H^+]C_L + \beta_{101}\alpha_2 C_L - 1 - \beta_{111}\alpha_2[H^+]C_{Eu} - \beta_{101}\alpha_2 C_{Eu})[L_\nu] + (\beta_{122}\alpha_2^2[H^+]^2 C_L + \beta_{112}\alpha_2^2[H^+]C_L - \beta_{111}\alpha_2[H^+] - \beta_{101}\alpha_2 - 2\beta_{122}\alpha_2^2[H^+]^2 C_{Eu} - 2\beta_{112}\alpha_2^2[H^+]C_{Eu})[L_\nu]^2 + (\beta_{123}\alpha_2^3[H^+]^2 C_L - \beta_{122}\alpha_2^2[H^+] - \beta_{112}\alpha_2^2[H^+] - 3\beta_{123}\alpha_2^3[H^+]^2 C_{Eu})[L_\nu]^3 - (\beta_{123}\alpha_2^3[H^+]^2)[L_\nu]^4 = 0 \quad (2)$$

β_{mhx} are the global formation constants of the complexes, where m is the number of Eu^{3+} ions, h the number of protons, and x the number of H_2L^{2-} ions. We consider H_2L^{2-}, since HL^{3-} and L^{4-} do not exist at pH < 2.

This method is useful in choosing the conditions for the preparation of solutions that contain a specified complex of optimal concentration compared to the other species. From the overall absorption spectrum of solutions with optimized concentration ratios of Eu/HEDP and pH, the spectra of the different complexes can be easily deduced.

4.2. Intensity Calculations. Experimental dipole strength values (D_{exp}) are determined by integrating the absorption peaks

$$D_{exp} = \frac{1}{108.9}\frac{g_i}{X_i(T)}\int \frac{\epsilon(\bar{\nu})}{\bar{\nu}} d\bar{\nu} \quad (3)$$

$\epsilon(\bar{\nu})$ is the molar absorption coefficient at wavenumber $\bar{\nu}$. When $\epsilon(\bar{\nu})$ is expressed in L mol^{-1} cm^{-1}, eq 3 gives values for the dipole strength in $Debye^2$. This equation is valid for solutions or randomly oriented systems in general. The initial state is characterized by a degeneracy g_i and a fractional thermal (Boltzmann) population $X_i(T)$. For the Eu^{3+} ion at room temperature this population factor has to be considered.

Intensity calculations are expressed in terms of magnetic dipole (MD) and electric dipole (ED) matrix elements, respectively $\langle\psi_i|O_{MD}|\psi_f\rangle$ and $\langle\psi_i|O_{ED}|\psi_f\rangle$. To calculate the dipole strength of a MD or an induced ED transition, these matrix elements have to be calculated. Whereas $\langle\psi_i|O_{MD}|\psi_f\rangle$ can be calculated exactly when appropriate wave functions are available, this is not the case for $\langle\psi_i|O_{ED}|\psi_f\rangle$. $\langle\psi_i|O_{ED}|\psi_f\rangle$ is commonly treated parametrically in the framework of the Judd−Ofelt theory.[9−11]

In this theory the expression for the calculated dipole strength for ED transitions becomes

$$D_{calc}^{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle\Psi_{\tau SLJ}||U^{(\lambda)}||\Psi_{\tau' S'L'J'}\rangle|^2 \quad (4)$$

with $e = -4.803 \times 10^{-10}$ esu. Ω_λ are the intensity parameters (in cm^2), which are deduced from the experimental values of the dipole strengths. The meaning of an intensity parameter is the square of the charge displacement due to the induced electric dipole transition. The reduced matrix elements, $|\langle\Psi_{\tau SLJ}||U^{(\lambda)}||\Psi_{\tau' S'L'J'}\rangle|^2$ are also written as $|U^\lambda|^2$.

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(10) Ofelt, G. S. *J. Chem. Phys.* **1962, *37***, 511.

(11) Görller-Walrand, C.; Binnemans, K. Spectral Intensities of f−f Transitions. In *Handbook on the Physics and Chemistry of Rare Earths*; Gscheidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1998; Vol. 25, Chapter 167.

The intensity parameters are determined using the expression

$$D_{\mathrm{exp}} = \frac{\chi^{\mathrm{ED}}}{2\mathrm{J}+1} e^2 (\Omega_2 |U^2|^2 + \Omega_4 |U^4|^2 + \Omega_6 |U^6|^2) + \chi^{\mathrm{MD}} D^{\mathrm{MD}}_{\mathrm{calc}} \tag{5}$$

Equation 5 shows that a transition can have both an induced ED and a MD contribution. Therefore the experimental dipole strength cannot be compared directly with the calculated dipole strength. χ^{ED} and χ^{MD} are correction factors that make allowance for the refractive index n of the medium in which the lanthanide ions are embedded. They are equal respectively to $(n^2 + 2)/9n$ and n. The refractive index for a $NaNO_3$ solution is $n = 1.4$. To calculate the intensity parameters in the case of Eu^{3+}, transitions that have only an induced ED contribution are used.

For the Eu(H_3L)(H_2L) complex in silicone grease neither the concentration nor the refractive index of the sample is known. For this sample the absorption peaks are integrated as follows:

$$A_{\mathrm{exp}} = \frac{1}{108.9} \frac{g_i}{\chi_i(T)} \int \frac{A(\bar{\nu})}{\bar{\nu}} \mathrm{d}\bar{\nu} \tag{6}$$

where $A(\bar{\nu})$ is equal to $cd\epsilon(\bar{\nu})$. The value of the dipole strength (A_{exp}, Debye^2 L mol^{-1} cm^{-1}) still depends on the concentration and the refractive index of the sample.

5. Results and Discussion

5.1. Eu(H$_3$L)(H$_2$L) Complex. The absorption spectrum at 4.2 K and the luminescence spectrum at room temperature (the excitation wavelength is 395 nm, $^5L_6$) of the Eu(H_3L)(H_2L) complex are used to determine the energy levels. It is assumed that the crystal structure remains the same at both temperatures. The positions of 10 free ion levels are deduced. Only eight crystal field levels could be determined: one for the $^5D_0$ free ion level, three for the $^5D_1$ level, and four for the $^5D_2$ level.

A mean set of free ion parameters for the Eu^{3+} ion is used as starting values to calculate the free ion levels.[12] These free ion levels are fitted to nine experimental free ion levels. Only six free ion parameters are varied and not all at the same time. The F^0 parameter of eq 1 is part of the sphere symmetric parameter (E_{AVG}), which is set to vary at each iteration.

The spin–orbit coupling parameter does not influence much the position of the $^5D_1$ and the $^5L_6$ level and therefore this parameter is being optimized using the other experimental free ion levels, ^7F_J, $^5D_0$, $^5D_2$, and $^5D_4$. On top of that, this parameter is the only one that has some influence on the position of the ^7F_J levels, and thus it is the most important free ion parameter.

Free ion levels that are experimentally observed originate from only three different ^{2S+1}L multiplets. Therefore the electron repulsion parameters are varied in a constant ratio at the beginning of the fitting procedure.[4] Later on, they are varied two at the time. The position of the $^5L_6$ level depends strongly on the α parameter, while the position of the other levels is merely independent of this parameter, which is the reason the $^5L_6$ energy level is the one that is best fitted.

Table 1. Free Ion Parameters (in cm^{-1}) for the Eu(H_3L)(H_2L) Complex

	free ion parameters		free ion parameters
E_{AVG}	63537	T^6*	−330
F^2	81578	T^7*	380
F^4	60268	T^8*	370
F^6	42472	ζ	1329
α	24.29	M^0*	2.38
$\beta*$	−617	M^2*	1.33
$\gamma*$	1460	M^4*	0.90
T^2*	370	P^2*	303
T^3*	40	P^4*	227
T^4*	40	P^6*	152

Table 2. Experimental and Theoretical Free Ion Energy Levels (in cm^{-1}) for the Eu(H_3L)(H_2L) Complex

free ion level	E_{exp}	E_{calc}	$E_{\mathrm{exp}} - E_{\mathrm{calc}}$
$^7F_0$	0	−52	52
$^7F_1$	304	324	−20
$^7F_2$	946	985	−39
$^7F_3$		1835	
$^7F_4$	2814	2807	7
$^7F_5$		3851	
$^7F_6$		4934	
$^5D_0$	17 276	17 285	−9
$^5D_1$	19 045	19 036	9
$^5D_2$	21 501	21 508	−7
$^5D_3$	24 384	24 392	−8
$^5L_6$	25 347	25 347	0
$^5G_2$		26 276	
$^5L_7$		26 403	
$^5G_3$		26 508	
$^5G_4$		26 638	
$^5G_5$		26 678	
$^5G_6$		26 687	
$^5L_8$		27 320	
$^5D_4$	27 632	27 626	6

Nine experimental free ion energy levels were used to determine the free ion parameters. At consecutive stages of the fitting procedure more parameters were allowed to vary freely, resulting in a set of parameters (Table 1) which is used to calculate the energy levels summarized in Table 2. The parameters with an asterix were constricted during the parametrization. A standard deviation $\sigma = 31$ cm^{-1} was reached, which is a satisfactory value since the small number of experimental energy levels to fit the parameters and because of the fact that it is a free ion fitting.

The positions of the ^5D_J and $^5L_6$ levels are in good agreement with the experimental data. The difference between the theoretical and experimental ^7F_J levels is larger, which is not so surprising, because these levels are not as sensitive to the variation of the parameters except for the variation of the spin–orbit coupling parameter. The position of the $^5D_3$ level was experimentally deduced from the position of the $^7F_1$ level, and this is why it is not implemented in the fitting procedure. Still, the theoretical $^5D_3$ level is in good agreement with this indirectly determined level.

Since lanthanide ions behave similarly in analogous compounds, the crystal field parameters of the Er^{3+} ion in the Er(H_3L)(H_2L) complex[3] are combined with the optimized free ion parameters of Table 1 to calculate the crystal field levels of the Eu(H_3L)(H_2L) complex. To do so the Hamiltonian of eq 1 is expanded with the term

$$\sum_{k,q} B^k_q C^k_q$$

The coordination polyhedron of the Er^{3+} ion in the Er(H_3L)(H_2L) complex can be described by C_{2v} symmetry. The crystal field parameters describe mainly the influence of the surrounding of the lanthanide ion on the position of the crystal field levels. If the site symmetry of the Eu^{3+} ion in the Eu(H_3L)(H_2L)

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(12) Görller-Walrand, C.; Binnemans, K., Rationalization of Crystal-field Parametrization. In *Handbook on the Physics and Chemistry of Rare Earths*; *Gschneidner, K. A., Jr., and Eyring, L.*, Eds.; North-Holland: Amsterdam, 1996; Vol. 23, Chapter 155.

Table 3. Calculated and Experimental Crystal Field Levels (in cm^{-1})

free ion level	E_{exp}	E_{calc}	$E_{exp} - E_{calc}$	symmetry label in C_{2v}
$^5D_0$	17 276.0	17 281.2	−5.2	Γ_1
$^5D_1$	19 018.0	19 013.6	4.4	Γ_2 or Γ_4
	19 044.0	19 039.2	4.8	Γ_3
	19 072.0	19 044.1	27.9	Γ_2 or Γ_4
$^5D_2$	21 461.0	21 473.3	−12.3	Γ_1
	21 480.0	21 473.4	6.6	Γ_2 or Γ_4
	21 516.0	21 515.3	0.7	Γ_2 or Γ_4
		21 525.2		Γ_3
	21 549.0	21 535.1	13.9	Γ_1

complex is the same as the site symmetry of the Er^{3+} ion in the same complex, as can be suspected because of the similar ionic radius of both ions and the tendency of both complexes to form needles, the crystal field parameters that describe the site symmetry in the Er^{3+} complex should also describe the site symmetry of $Eu(H_3L)(H_2L)$. The experimental and the calculated crystal field levels are listed in Table 3. As can be seen in the table, the experimental and calculated energy levels are in good agreement. The symmetry labels of these energy levels are deduced from the crystal field quantum number, μ.[13] The mixing crystal field levels are Γ_1 and Γ_3 for crystal field quantum number $\mu = 0$, and Γ_2 and Γ_4 for $\mu = 1$. From the comparison of the eight experimental crystal field levels with the calculated energy levels (Table 3), one can conclude that the crystal field parameters are transferable from Er^{3+} to Eu^{3+} in the $Ln(H_3L)(H_2L)$ complexes and this indicates that the site symmetry of the Eu^{3+} ion in this complex can be described by a C_{2v} symmetry.

5.2. Eu^{3+}−HEDP Complexes in Solution. Figure 2 shows the absorption spectra of the Eu^{3+}−HEDP complexes in 2 M $NaNO_3$ (middle) together with the absorption spectrum of the Eu^{3+} ion in a 2 M $NaNO_3$ solution (bottom) and the spectrum of the $Eu(H_3L)(H_2L)$ complex in silicone grease (top) in the wavelength region 21 000−22 000 cm^{-1}. The ordinate in these spectra is in molar absorptivity, except for the top. There it is in arbitrary units (absorbance) since the concentration and the refractive index for this sample is unknown. The absorption spectrum of the $Eu(H_2L)^+$ complex could not be obtained, since a solution with a large enough concentration of this complex for absorption spectroscopy could not be made without precipitation of the $Eu(H_3L)(H_2L)$ solid complex. This figure shows a close resemblance of the spectra of the solid $Eu(H_3L)(H_2L)$ and the anionic $Eu(H_3L)_2(H_2L)^-$ complex, which suggests that the site symmetry around the Eu^{3+} ion in these complexes is similar. The same can be said for the site symmetry around the Eu^{3+} ion in 2 M $NaNO_3$ and the site symmetry of the Eu^{3+} ion in the two cationic complexes, $Eu(H_3L)^{2+}$ and $Eu(H_3L)_2{}^+$, so the close resemblance found for the spectrum of the Eu^{3+} ion and those of the two cationic complexes indicates that the site symmetry of Eu^{3+} for these two species must be the same. The same deduction can be made for the other spectral regions showing the other transitions, but the resemblance of the spectra is the most explicit for the $^5D_2 \leftarrow {}^7F_0$ transition.

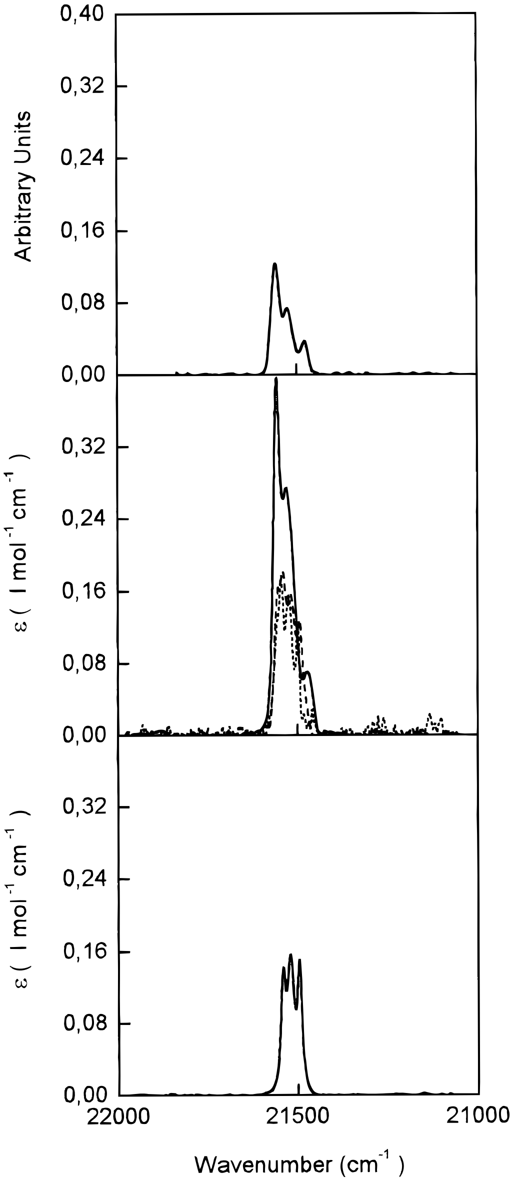

Figure 2. Absorption spectra (21 000−22 000 cm^{-1}) of the different complexes in solid state and in 2 M $NaNO_3$ solution, showing the $^5D_2 \leftarrow {}^7F_0$ transition, $T = 293$ K. Top: $Eu(H_3L)(H_2L)$ in silicone grease. Middle: $Eu(H_3L)^{2+}$, $Eu(H_3L)_2{}^+$, and $Eu(H_3L)_2(H_2L)^-$ in 2 M $NaNO_3$. Bottom: Eu^{3+} in 2 M $NaNO_3$.

Table 4. Reduced Matrix Elements for Eu^{3+} for Transitions Starting in the $^7F_0$ Level

free ion level	energy	$\lvert U^2\rvert^2$	$\lvert U^4\rvert^2$	$\lvert U^6\rvert^2$
$^5D_2$	21 508	0.000 800 2	0	0
$^5L_6$	25 391	0	0	0.015 761 4
$^5G_2$	26 369	0.000 564 4	0	0
$^5G_4$	26 797	0	0.000 717 1	0
$^5G_6$	26 864	0	0	0.003 590 7
$^5D_4$	27 619	0	0.001 117 6	0

The reduced matrix elements, $|U^\lambda|^2$, calculated with the free ion parameter set that was optimized for the $Eu(H_3L)(H_2L)$ complex, are listed in Table 4. Experimental dipole strength values (D_{exp}) of the complexes in solution and experimental relative dipole strength values (A_{exp}) of the $Eu(H_3L)(H_2L)$ complex in silicone grease are listed in Table 5, as are the calculated dipole strengths of the complexes in solution. The intensity parameters used to calculate the D^{calc} in Table 5 are given in Table 6.

The intensity of induced ED transitions are normally not much affected by the surroundings of a lanthanide ion. Still there are some transitions, called hypersensitive transitions, that are very sensitive for the environment, and these are usually more intense when the lanthanide ion is complexed than when the

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(13) Wybourne, B. *Spectroscopic Properties of Rare Earths*; John Wiley and Sons: New York, 1965.

Table 5. A_{exp} for the $Eu(H_3L)(H_2L)$ Complex in Silicone Grease, D_{exp} and D_{calc} for the Complexes in 2 M $NaNO_3$ ($T = 293$ K)

transition	A_{exp}	D_{exp}	D_{calc}	$\frac{D_{calc}}{D_{exp}}$	D_{exp}	D_{calc}	$\frac{D_{calc}}{D_{exp}}$
	$Eu(H_3L)(H_2L)$		Eu^{3+}			$Eu(H_3L)^{2+}$	
$^5D_0 \leftarrow {}^7F_1$		9.62	13.1	1.36			
$^5D_0 \leftarrow {}^7F_0$		0.11					
$^5D_1 \leftarrow {}^7F_1$	1.43	13.4	19.0	1.42			
$^5D_1 \leftarrow {}^7F_0$	1.71	2.34	2.54	1.09	2.29	2.54	1.11
$^5D_2 \leftarrow {}^7F_0$	5.04	5.89	5.89	1	8.60	8.60	1
$^5D_3 \leftarrow {}^7F_1$	15.4	20.61	23.36	1.13			
$^5L_6 \leftarrow {}^7F_0$	57.78	242.25	242.25	1	232.84	232.84	1
$^5G_J \leftarrow {}^7F_0$	32.67	71.7	71.32	0.99	60.77	71.63	1.18
$^5D_4 \leftarrow {}^7F_1$		13.51	11.90	0.88			
$^5D_4 \leftarrow {}^7F_0$	10.15	18.66	18.66	1	19.51	19.51	1
			$Eu(H_3L)_2{}^+$			$Eu(H_3L)_2(H_2L)^-$	
$^5D_0 \leftarrow {}^7F_0$					0.15		
$^5D_1 \leftarrow {}^7F_0$		2.38	2.54	1.09	2.44	2.54	1.05
$^5D_2 \leftarrow {}^7F_0$		6.93	6.93	1	15.16	15.16	1
$^5L_6 \leftarrow {}^7F_0$		235.46	235.46	1	221.80	221.80	1
$^5G_J \leftarrow {}^7F_0$		87.69	75.68	0.87	57.47	75.07	1.31
$^5D_4 \leftarrow {}^7F_0$		20.18	20.18	1	21.57	21.57	1

[a] A_{exp} is in 10^{-6} Debye^2 L mol^{-1} cm^{-1}, and D_{exp} and D_{calc} are in 10^{-6} Debye^2.

Table 6. Intensity Parameters for the Eu^{3+} Complexes in Solution ($\times 10^{-20}$ cm^2)

complex	Ω_2	Ω_4	Ω_6
Eu^{3+}	2.56	5.82	5.35
$Eu(H_3L)^{2+}$	3.74	6.08	5.15
$Eu(H_3L)_2{}^+$	3.01	6.29	5.20
$Eu(H_3L)_2(H_2L)^-$	6.60	6.72	4.90

Table 7. Ratios of the Experimental Dipole Strengths (D_{exp}) for the Complexes in Solution and Ratios of the Relative Dipole Strengths (A_{exp}) for the $Eu(H_3L)(H_2L)$ Complex

complex	$\frac{^5L_6 \leftarrow {}^7F_0}{^5D_2 \leftarrow {}^7F_0}$	$\frac{^5G_J \leftarrow {}^7F_0}{^5D_2 \leftarrow {}^7F_0}$	$\frac{^5D_4 \leftarrow {}^7F_0}{^5D_2 \leftarrow {}^7F_0}$
Eu^{3+}	41.10	12.17	3.17
$Eu(H_3L)^{2+}$	27.07	7.07	2.27
$Eu(H_3L)_2{}^+$	34.98	12.65	2.91
$Eu(H_3L)(H_2L)$	9.54	4.55	1.97
$Eu(H_3L)_2(H_2L)^-$	14.63	3.79	1.42

ion is in an aqueous solution. The site symmetry of Eu^{3+} in the complexes is discussed using the hypersensitive transition, $^5D_2 \leftarrow {}^7F_0$. Figure 2 shows that the intensity of this transition is the largest in the spectrum of the $Eu(H_3L)_2(H_2L)^-$ complex. To compare the intensity of this transition in the spectra of the different complexes, one should compare the experimental dipole strength of this hypersensitive transition to the experimental dipole strength of the symmetry independent MD transitions. This cannot be done for the $Eu(H_3L)(H_2L)$ solid complex, because the refractive index of this sample is unknown. Therefore, the experimental dipole strength of this hypersensitive transition is compared to the experimental dipole strength of the other, less symmetry dependent, ED transitions. The refractive index can be excluded out of the ratios listed in Table 7. This table shows decreasing values for the ratios: $Eu^{3+} < Eu(H_3L)^{2+} < Eu(H_3L)_2{}^+ < Eu(H_3L)(H_2L)$ and $Eu(H_3L)_2(H_2L)^-$. This indicates that the aqueous surrounding of the Eu^{3+} ion is being replaced by the strongly complexing HEDP molecules, going from the Eu^{3+} ion in 2 M $NaNO_3$ over the $Eu(H_3L)^{2+}$ and $Eu(H_3L)_2{}^+$ complex to the $Eu(H_3L)(H_2L)$ and $Eu(H_3L)_2(H_2L)^-$ complexes.

6. Conclusions

The complexation of the Eu^{3+} ion by HEDP is investigated in the solid state as well as in solution. Because of the limited number of experimentally observed energy levels in the spectrum of the Eu^{3+}-HEDP complex in the solid state, only the free ion parameters were optimized by the fitting procedure. The crystal field parameters, which describe the symmetry around the lanthanide ion, are taken from the complex of Er^{3+} with HEDP to calculate the crystal field energy levels. The good agreement of the calculated crystal field levels with the experimentally observed crystal field levels indicates that the symmetry surrounding the Eu^{3+} ion approximates the C_{2v} symmetry as well. The spectrum of the Eu^{3+}−HEDP complex is compared with the spectra of two positively charged complexes and one negatively charged complex of HEDP with Eu^{3+} in a 2 M $NaNO_3$ solution. The spectrum of the negatively charged complex in solution was found to be similar to that of the complex in solid state, which points out that the symmetry surrounding the Eu^{3+} ion in both complexes is similar.

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