6624 *J. Phys. Chem. A* **2004,** *108,* 6624−6628

Spectroscopic Evidence for Equilibrium between Eight- and Nine-Coordinate Eu^{3+}(aq) Species in 0.1 M $EuCl_3$(aq)

Lisa Tilkens, Kristen Randall, Jian Sun, Mary T. Berry, and P. Stanley May*

Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069

Toshihiro Yamase

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

Received: January 28, 2004; In Final Form: June 9, 2004

Crystalline europium bromate, $[Eu(H_2O)_9][(BrO_3)_3]$, europium ethyl sulfate, $[Eu(H_2O)_9][(C_2H_5SO_4)_3]$, and europium decavanate, $[Eu(H_2O)_8]_2[(V_{10}O_{28})]\cdot 8H_2O$, are used as models for nine- and eight-coordinate Eu^{3+} aquo species in solution. A comparison of the $^5D_1 \leftarrow {}^7F_0$ laser excitation spectra and $D_0 \rightarrow {}^7F_{1,2}$ emission spectra of the model crystal systems with that of 0.1 M $EuCl_3$(aq) clearly indicates a significant presence of the $Eu(H_2O)_8{}^{3+}$ species in aqueous solution. Modeling the 0.1 M $EuCl_3$(aq) spectra using weighted sums of the eight and nine-coordinate crystal spectra suggest that approximately two-thirds of Eu^{3+} ions exist as $Eu(H_2O)_8{}^{3+}$ in aqueous solution. The current study takes advantage of the symmetry of the $Eu(H_2O)_n{}^{3+}$ complexes and lends further support, from this perspective, that an equilibrium exists between $Eu(H_2O)_8{}^{3+}$ and $Eu(H_2O)_9{}^{3+}$, with significant representation from both species.

1. Introduction

The nature of the water coordination for Eu^{3+} ions in dilute aqueous solution with noncoordinating counterions has been much debated. Measurements based on the luminescence lifetime of the $^5D_0$ state suggest a coordination number of 9.2 ± 0.5.[1] Various molecular dynamics simulations have predicted pure nine-coordinate species[2], eight-coordinate species[3], or an equilibrium with nearly equal concentrations of the two.[4] A thermodynamic calculation by Miyakawa et al.[5] for the equilibrium

$$Eu(H_2O)_9(aq) \leftrightarrow Eu(H_2O)_8(aq) + H_2O(l)$$

gives $\Delta G = -1.0$ kJ/mol and $K = 1.5$ at 298 K, implying an average coordination number of 8.4. The X-ray diffraction studies of Habenschuss and Spedding on 3 M $EuCl_3$ also support an equilibrium between the two species with an average coordination number of 8.3.[6] The validity of extending the 3 M results to coordination in dilute solution was challenged with the suggestion that inner sphere coordination of Eu^{3+} by Cl^- could lower the water coordination at high chloride concentration.[7] However, interpolating the neutron diffraction data of Cossy et al. for water coordination in the more dilute, 1 and 0.3 M Nd^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} also supports an intermediate water coordination number for Eu^{3+}.[8] Thus, although the preponderance of evidence is indeed for equilibrium between eight- and nine-coordinate europium aquo species, the question does not appear to have been entirely resolved.[9]

The crystal-field splitting of the Eu^{3+} ^7F_J and ^5D_J multiplets is generally quite sensitive to the symmetry and nature of the inner sphere coordination and relatively insensitive to outer sphere effects. In the molecular dynamics calculations the eight coordinate aqueous species is consistently predicted to exhibit a square antiprism geometry and the nine coordinate, a tricapped trigonal prism geometry. Thus, it would seem likely that europium ethyl sulfate, $[Eu(H_2O)_9][(C_2H_5SO_4)_3]$, and europium bromate, $[Eu(H_2O)_9][(BrO_3)_3]$, both of which incorporate tricapped trigonal prismatic $Eu(H_2O)_9{}^{3+}$ units,[10] would serve as good models for the luminescence characteristics of aqueous $Eu(H_2O)_9{}^{3+}$ and that europium decavanadate, $[Eu(H_2O)_8]_2[(V_{10}O_{28})]\cdot 8H_2O$,[11] which exhibits eight-coordinate square antiprismatic $Eu(H_2O)_8{}^{3+}$ units would serve as a good model for aqueous $Eu(H_2O)_8{}^{3+}$. In this paper we present a spectroscopic comparison of the crystalline and aqueous systems and the strong evidence therein further supporting an equilibrium between eight- and nine-coordinate aqueous species.

2. Experimental Section

Polycrystalline samples of europium ethyl sulfate (EuES) and europium bromate (EuB) were prepared using published methods.[10,12] Europium decavanadate, (EuDV) was provided by Professor Toshihiro Yamase at the Tokyo Institute of Technology. The identity of the EuES was confirmed by comparison to published luminescence spectra.[13] The identities of the EuB and EuDV were confirmed by powder X-ray diffraction.

Luminescence spectra for the three crystalline systems and for 0.1 M $EuCl_3$ were obtained on the $^5D_1 \leftarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_{1,2}$ transitions using standard methods of laser induced fluorescence with equipment described previously.[14] The spectra for EuDV were measured at low temperature (8 K) to minimize the strong absorbance of the anion. All other measurements were made at room temperature.

EuES and EuB both have a single Eu^{3+} site in the crystal structure. In the EuDV crystal there are two Eu^{3+} sites. Both EuDV sites have square antiprism geometries, but the two are sufficiently different to show a small difference in the crystal-field splitting as well as a wavelength shift in the center of the multiplet to multiplet transitions. Emission spectra for the two

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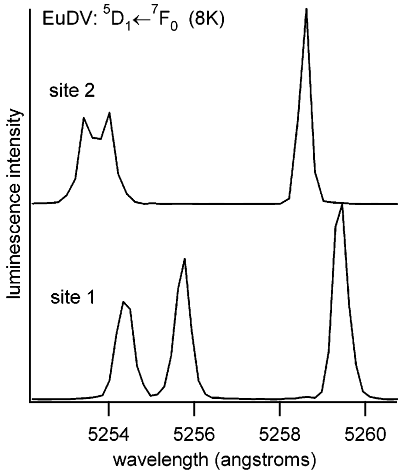

Figure 1. Site-selective $^5D_1 \leftarrow {}^7F_0$ laser excitation spectra at 8 K for the two distinct square antiprismatic $Eu(H_2O)_8^{3+}$ units of europium decavanadate (EuDV) powder. The spectra were obtained by monitoring $^5D_0 \rightarrow {}^7F_1$ emission with 2 Å resolution at 5897 Å for site 1 and 5892 Å for site 2.

sites were isolated with selective $^5D_1 \leftarrow {}^7F_0$ excitation at 5255.8 Å for site 1 and 5258.6 Å for site 2. Excitation spectra for the two sites were isolated through selective monitoring of $^5D_0 \rightarrow {}^7F_1$ emission with 2 Å resolution at 5897 Å for site 1 and 5892 Å for site 2.

3. Results and Discussion

3.1. $[Eu(H_2O)_8]_2[(V_{10}O_{28})]\cdot 8H_2O$ Spectra. EuDV is the first reported compound with an $[Eu(H_2O)_8]^{3+}$ unit which has been crystallographically characterized. Because there have been no previous reports of site-selective spectroscopy on this compound, we will briefly discuss our results before proceeding to the comparative aspects of our study.

The $^5D_1 \leftarrow {}^7F_0$ excitation spectra (8 K) of the two Eu^{3+} sites in EuDV are shown in Figure 1. With perfect D_{4d} symmetry, each spectrum would exhibit two features, representing transitions to the A_2 and E_3 crystal-field components of $^5D_1$. Of the three peaks actually observed, the two closely spaced peaks on the left side of both spectra can be viewed as resulting from the splitting of the E_3 component due to distortion of the $[Eu(H_2O)_8]^{3+}$ complexes from D_{4d}. Following this reasoning, we tentatively assign the lower spectrum in Figure 1, which has the larger E_3 splitting, to the more distorted of the two complexes (site 1). The coordination geometries for both sites in EuDV, as determined by X-ray crystallography, are graphically depicted in ref 11.

The $^5D_0 \rightarrow {}^7F_{1,2}$ emission spectra (8 K) of the two Eu^{3+} sites in EuDV are shown in Figure 2. Again, the two closely spaced peaks in the $^5D_0 \rightarrow {}^7F_1$ region can be viewed as resulting from the splitting of the E_3 component of $^7F_1$. The larger splitting observed for site 1 is consistent with our analysis of the $^5D_1 \leftarrow {}^7F_0$ excitation spectra, and further supports site 1 as the more distorted of the two sites.

3.2. Comparison of Eu^{3+} $^5D_1 \leftarrow {}^7F_0$ Excitation Spectra. A comparison of the $^5D_1 \leftarrow {}^7F_0$ excitation spectra for 0.1 M $EuCl_3$(aq) with the $Eu(H_2O)_8^{3+}$ and $Eu(H_2O)_9^{3+}$ model crystal systems is shown in Figure 3. The crystal spectra have been wavelength-shifted, as indicated, to facilitate comparison of the splitting pattern and relative intensities of the crystal-field transitions. The slight variation in the multiplet-to-multiplet transition energies seen in Figure 3 is typical, and reflects differences in the *isotropic* contribution to electrostatic repulsion from the host.

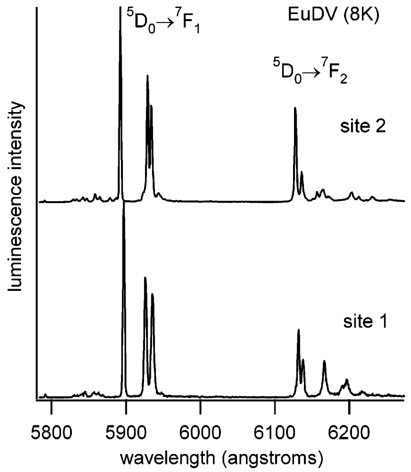

Figure 2. Site-selective $D_0 \rightarrow {}^7F_{1,2}$ emission spectra at 8 K for the two distinct square antiprismatic $Eu(H_2O)_8^{3+}$ units of europium decavanadate (EuDV) powder. The spectra were obtained by laser excitation into the $^5D_1 \leftarrow {}^7F_0$ region at 5255.8 Å for site 1 and 5258.6 Å for site 2.

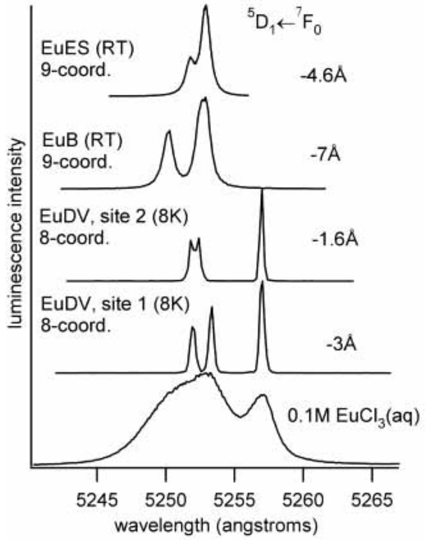

Figure 3. Comparison of the $^5D_1 \leftarrow {}^7F_0$ laser excitation spectra of the nine- and eight-coordinate model crystal compounds with that of the aquo complex in 0.1 M $EuCl_3$. The crystal spectra have been wavelength-shifted, as indicated, to facilitate comparison. The EuDV spectra were obtained as described in Figure 1. The EuES, EuB, and 0.1 M $EuCl_3$(aq) spectra were obtained by monitoring Eu^{3+} $^5D_0 \rightarrow {}^7F_1$ emission at 5915, 5912, and 5920 Å, respectively.

It is the splitting patterns and relative intensities of the crystal-field transitions that are most characteristic of the coordination geometry. Clearly, the spectra for nine-coordinate species do not closely resemble the spectra for $Eu(aq)^{3+}$. The overall crystal-field splitting of the $^5D_1$ multiplet is much larger in the aqueous spectrum, and there are three distinct features in the aquo spectrum, whereas the nine-coordinate spectra exhibit only two. In fact, the aquo spectrum looks most similar to the $Eu(H_2O)_8^{3+}$ complex (site 1) of EuDV. A qualitative visual comparison of these spectra strongly suggests the presence of a significant fractional population of $Eu(H_2O)_8^{3+}$ in 0.1 M $EuCl_3$(aq).

Figure 4 shows a comparison of the 0.1 M $EuCl_3$(aq) spectrum with artificially broadened nine-coordinate (EuB) and eight-coordinate (EuDV, site 1) model crystal spectra. The broadened crystal spectra were produced from the spectra in Figure 3 by applying a Gaussian smoothing routine. This

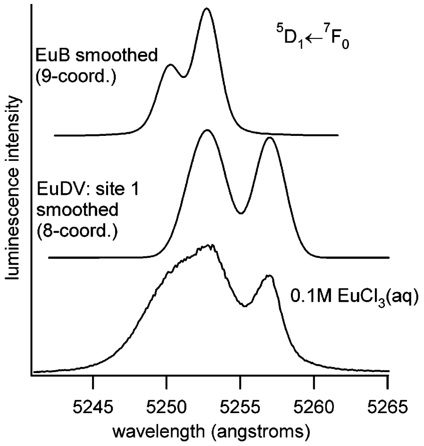

Figure 4. Comparison of the $^5D_1 \leftarrow {}^7F_0$ laser excitation spectra of artificially broadened nine- and eight-coordinate model crystal compounds with that of the aquo complex in 0.1 M EuCl$_3$. The broadened crystal spectra were obtained by applying a Gaussian smoothing routine to the spectra in Figure 3. The wavelength shifts are the same as in Figure 3.

comparison is useful because it clearly suggests how the EuCl$_3$(aq) spectrum might be described in terms of a superposition of Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra.

Because the $^5D_1 \leftarrow {}^7F_0$ transition is almost purely magnetic dipole, its integrated intensity is relatively insensitive to the crystal-field environment. If, therefore, the 0.1 M EuCl$_3$(aq) spectrum can be fit to a linear combination of Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra, the fractional contribution of each species to the integrated intensity of the 0.1 M EuCl$_3$(aq) spectrum will approximately equal its fractional population in aqueous solution.

To obtain a semiquantitative estimate of the relative populations of the Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ species in aqueous solution, we fit the 0.1 M EuCl$_3$(aq) spectrum to simulated eight- and nine-coordinate model spectra. Each model spectrum was represented as a linear combination of Gaussian functions. The splittings and relative intensities of the crystal-field transitions of the nine-coordinate model spectrum were assigned the average values observed for EuES and EuB. Similarly, the splittings and relative intensities of the crystal-field transitions of the simulated eight-coordinate model spectrum were assigned the average values observed for site 1 and site 2 of EuDV. The widths of the Gaussian peaks were assigned by visual inspection, because it was clear that simulated spectra could not describe the shape of the “wings” of the 0.1 M EuCl$_3$(aq) spectrum.[15] The line width of each individual crystal-field transition was assigned the same value. The best fit was obtained by wavelength-shifting and scaling the relative contributions of the simulated Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra. The wavelength scale was converted to wavenumbers (cm^{-1}) for the fitting procedure.

The form of the fit equation is given by

$$I(\bar{\nu}) = K_8[0.24e^{-(\bar{\nu}-\bar{\nu}_1-a)^2/2\sigma} + 0.27e^{-(\bar{\nu}-\bar{\nu}_2-a)^2/2\sigma} + 0.48e^{-(\bar{\nu}-\bar{\nu}_3-a)^2/2\sigma}] + K_9[0.33e^{-(\bar{\nu}-\bar{\nu}_4-b)^2/2\sigma} + 0.67e^{-(\bar{\nu}-\bar{\nu}_5-b)^2/2\sigma}] \quad (1)$$

where K_8 and K_9 are adjustable parameters that scale the relative contributions of the Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra, respectively, $\bar{\nu}_1$ through $\bar{\nu}_3$ are the peak positions (in cm^{-1}) of the crystal-field transitions for Eu(H$_2$O)$_8^{3+}$, $\bar{\nu}_4$ and $\bar{\nu}_5$ are the peak positions (in cm^{-1}) of the crystal-field transitions for Eu(H$_2$O)$_8^{3+}$, a and b are adjustable parameters for energy-shifting the Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra, respectively, and σ determines the line widths of the crystal-field transitions. The final set of parameters used to model the 0.1 M EuCl$_3$(aq) spectra are given in Table 1.

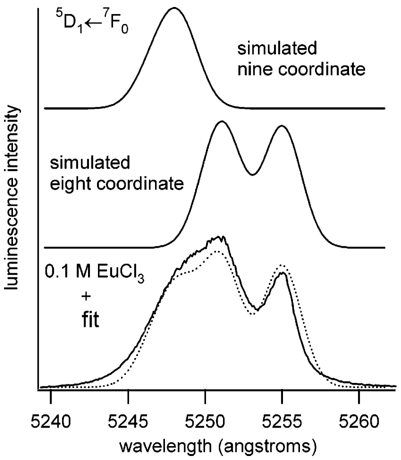

Figure 5. Fit of the $^5D_1 \leftarrow {}^7F_0$ laser excitation spectrum 0.1 M EuCl$_3$ using a linear combination of simulated Eu(H$_2$O)$_8^{3+}$ and Eu(H$_2$O)$_9^{3+}$ spectra. The top two spectra show the individual contributions of the nine- and eight-coordinate model spectra to the fit. The sum of the simulated spectra (dotted line) is overlaid with the observed 0.1 M EuCl$_3$(aq) spectrum at the bottom of the figure. A description of the fitting procedure is given in section 3.2.

The results of the fit are shown in Figure 5. The top two spectra show the individual contributions of the nine- and eight-coordinate model spectra to the fit. The sum of the simulated spectra (dotted line) is overlaid with the observed 0.1 M EuCl$_3$(aq) spectrum at the bottom of Figure 5. The fitted spectrum gives a quite reasonable representation of the observed spectrum of the Eu^{3+} aquo complex. The relative integrated intensities of the simulated spectra suggest that ~67% of Eu^{3+} ions exist as Eu(H$_2$O)$_8^{3+}$ in 0.1 M EuCl$_3$(aq). This result is similar to the X-ray diffraction value of ~70% Eu(H$_2$O)$_8^{3+}$ reported by Habenschuss and Spedding,[6] the calculated thermodynamic value of ~60% reported by Miyakawa,[5] and with the trends observed in the neutron diffraction data of Cosy et al.[8] and in the molecular dynamics calculations of Kowall et al.[4]

The uncertainty in our fitting analysis is due mainly to the uncertainties associated with assigning crystal-field splittings and relative intensities in the 8- and 9-coordinate model spectra represented in eq 1. We have assessed the sensitivity of our analysis to these assignments by using the observed splittings and relative intensities for the two 8-coordinate EuDV sites and the two 9-coordinate compounds (EuES and EuBrO$_3$) in eq 1 in all four possible combinations. The average of these four fits yields 69.4 ± 5.0% Eu(H$_2$O)$_8^{3+}$. Therefore, although the quantitative results are somewhat sensitive to the uncertainties inherent in the model, they consistently support a preponderance of Eu(H$_2$O)$_8^{3+}$.

3.3. Comparison of Eu^{3+} $^5D_0 \rightarrow {}^7F_{1,2}$ Emission Spectra.

A comparison of the $^5D_0 \rightarrow {}^7F_{1,2}$ emission spectra for 0.1 M

TABLE 1: Parameter Values for Eq 1 Used To Generate the Simulated $^5D_1 \leftarrow {}^7F_0$ Excitation Spectrum for 0.1 M EuCl$_3$ Shown in Figure 5

($\bar{\nu}_1$ + a)	($\bar{\nu}_2$ + a)	($\bar{\nu}_3$ + a)	($\bar{\nu}_4$ + b)	($\bar{\nu}_5$ + b)	K_8/K_9	σ
19041 cm^{-1}	19038 cm^{-1}	19025 cm^{-1}	19054 cm^{-1}	19048 cm^{-1}	2.04	25 cm^{-1}

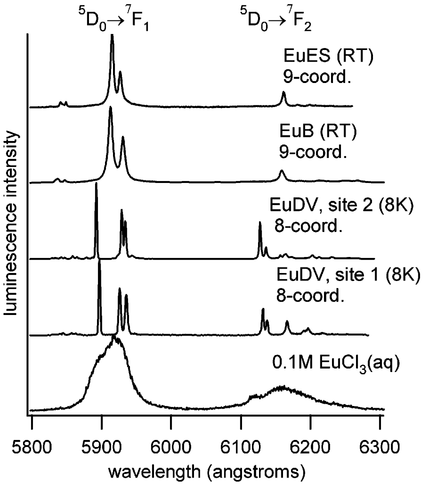

Figure 6. Comparison of the Eu^{3+} $^5D_0 \rightarrow {}^7F_{1,\,2}$ emission spectra of the nine- and eight-coordinate model crystal compounds with that of the aquo complex in 0.1 M $EuCl_3$. The EuDV spectra were obtained as described in Figure 2. The EuES and EuB spectra were obtained using $^5D_1$ laser excitation at 5252 and 5260 Å, respectively. The 0.1 M $EuCl_3(aq)$ spectrum was obtained using $^5D_2$ laser excitation at 4646 Å.

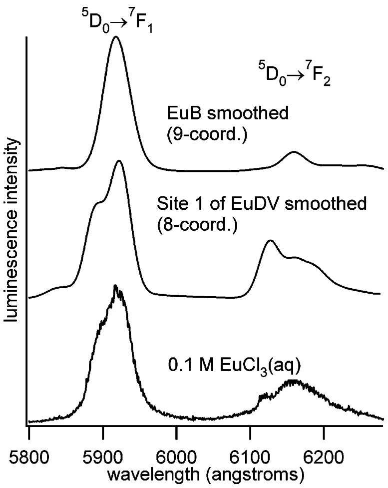

Figure 7. Comparison of the $^5D_0 \rightarrow {}^7F_{1,\,2}$ emission spectra of artificially broadened nine- and eight-coordinate model crystal compounds with that of the aquo complex in 0.1 M $EuCl_3$. The broadened crystal spectra were obtained by applying a Gaussian smoothing routine to the spectra in Figure 6.

$EuCl_3(aq)$ with the $Eu(H_2O)_8{}^{3+}$ and $Eu(H_2O)_9{}^{3+}$ model crystal systems is shown in Figure 6. Again, a visual comparison of these spectra strongly supports the presence of a significant fractional population of $Eu(H_2O)_8{}^{3+}$ in 0.1 M $EuCl_3(aq)$. This is particularly clear when the $^5D_0 \rightarrow {}^7F_2$ regions of the spectra are compared.

Figure 7 shows a comparison of the 0.1 M $EuCl_3(aq)$ spectrum with artificially broadened nine-coordinate (EuB) and eight-coordinate (EuDV, site 1) model crystal spectra. The broadened crystal spectra were produced from the spectra in Figure 6 by applying a Gaussian smoothing routine. It is remarkable how similar the 8-coordinate spectrum of EuDV (site 1) is to the aquo spectrum. Clearly, the 0.1 M $EuCl_3(aq)$ spectrum cannot be well represented solely in terms of a nine-coordinate spectrum.

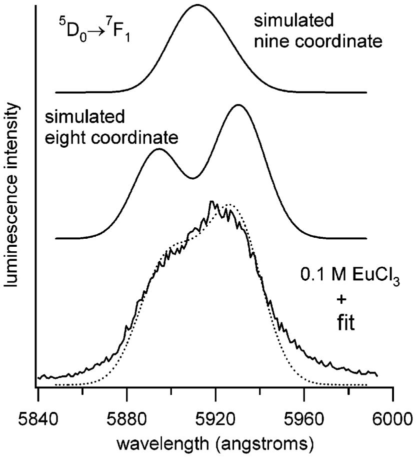

Figure 8. Fit of the $^5D_1 \leftarrow {}^7F_0$ laser excitation spectrum 0.1 M $EuCl_3$ using a linear combination of simulated $Eu(H_2O)_8{}^{3+}$ and $Eu(H_2O)_9{}^{3+}$ spectra. The top two spectra show the individual contributions of the nine- and eight-coordinate model spectra to the fit. The sum of the simulated spectra (dotted line) is overlaid with the observed 0.1 M $EuCl_3(aq)$ spectrum at the bottom of the figure. A description of the fitting procedure is given in sections 3.2 and 3.3.

As with the $^5D_1 \leftarrow {}^7F_0$ transition, $^5D_0 \rightarrow {}^7F_1$ emission intensity is almost purely magnetic-dipole. The 0.1 M $EuCl_3(aq)$ spectrum can, therefore, be fit to a linear combination of model $Eu(H_2O)_8{}^{3+}$ and $Eu(H_2O)_9{}^{3+}$ spectra to estimate the fractional population of each species in aqueous solution. The method used to perform this fit was very similar to that described in section 3.2 to produce the fit shown in Figure 5. The best fit was obtained by wavelength-shifting and scaling the relative contributions of the simulated $Eu(H_2O)_8{}^{3+}$ and $Eu(H_2O)_9{}^{3+}$ spectra.

$$I(\bar{\nu}) = K_8[0.39e^{-(\bar{\nu}-\bar{\nu}_1-a)^2/2\sigma} + 0.32e^{-(\bar{\nu}-\bar{\nu}_2-a)^2/2\sigma} + 0.29e^{-(\bar{\nu}-\bar{\nu}_3-a)^2/2\sigma}] + K_9[0.66e^{-(\bar{\nu}-\bar{\nu}_4-b)^2/2\sigma} + 0.34e^{-(\bar{\nu}-\bar{\nu}_5-b)^2/2\sigma}] \quad (2)$$

where the terms have the same meaning as in eq 1. The final set of parameters used to model the 0.1 M $EuCl_3(aq)$ spectra are given in Table 2.

The results of the fit are shown in Figure 8. The top two spectra show the individual contributions of the nine- and eight-coordinate model spectra to the fit. The sum of the simulated spectra (dotted line) is overlaid with the observed 0.1 M $EuCl_3(aq)$ spectrum at the bottom of Figure 5. As with our analysis of the $^5D_1 \leftarrow {}^7F_0$ excitation spectrum, the fitted spectrum yields a good representation of the observed spectrum of the Eu^{3+} aquo complex. The relative integrated intensities of the simulated spectra suggest that ~68% of Eu^{3+} ions exist as $Eu(H_2O)_8{}^{3+}$ in 0.1 M $EuCl_3(aq)$, which is in very good agreement with the result obtained from our analysis of the $^5D_1 \leftarrow {}^7F_0$ excitation spectrum in section 3.2.

As with our fitting of the $^5D_1 \leftarrow {}^7F_0$ 0.1 M $EuCl_3(aq)$ excitation spectrum in section 3.2, the uncertainty in the preceding analysis is due mainly to the uncertainties associated with assigning crystal-field splittings and relative intensities in the 8- and 9-coordinate model spectra. We have assessed the

TABLE 2: Parameter Values for Eq 2 Used To Generate the Simulated $^5D_1 \leftarrow {}^7F_0$ Excitation Spectrum for 0.1 M $EuCl_3$ Shown in Figure 8

$(\bar{\nu}_1 + a)$	$(\bar{\nu}_2 + a)$	$(\bar{\nu}_3 + a)$	$(\bar{\nu}_4 + b)$	$(\bar{\nu}_5 + b)$	K_8/K_9	σ
16966 cm^{-1}	16872 cm^{-1}	16851 cm^{-1}	16925 cm^{-1}	16882 cm^{-1}	2.17	1000 cm^{-1}

sensitivity of our analysis to these assignments by using the observed splittings and relative intensities for the two 8-coordinate EuDV sites and the two 9-coordinate compounds (EuES and $EuBrO_3$) in eq 2 in all four possible combinations. The average of these four fits yields 69.2 ± 9.6% $Eu(H_2O)_8^{3+}$. This compares well to the value of 69.4 ± 5.0% $Eu(H_2O)_8^{3+}$ obtained in section 3.2, although the standard deviation is significantly higher. It was noted that the fits to the 0.1 M $EuCl_3$(aq) $^5D_0 \rightarrow {}^7F_1$ emission spectrum were particularly sensitive to the total splitting in the eight-coordinate model spectrum.

4. Conclusions

Visual comparison of the $^5D_1 \leftarrow {}^7F_0$ excitation spectra and $D_0 \rightarrow {}^7F_{1,\,2}$ emission spectra of 0.1 M $EuCl_3$(aq) with model crystal systems in which the Eu^{3+} ion exists as either $Eu(H_2O)_8^{3+}$ or $Eu(H_2O)_9^{3+}$ complexes clearly suggests a significant presence of the $Eu(H_2O)_8^{3+}$ species in the aqueous solution. Modeling the 0.1 M $EuCl_3$(aq) $^5D_1 \leftarrow {}^7F_0$ excitation spectra using weighted sums of the eight- and nine-coordinate crystal spectra suggests that 69.4 ± 5.0% of Eu^{3+} ions exist as $Eu(H_2O)_8^{3+}$ in aqueous solution. Separate modeling of the 0.1 M $EuCl_3$(aq) $D_0 \rightarrow {}^7F_1$ emission spectra using weighted sums of the eight- and nine-coordinate crystal spectra indicates 69.2 ± 9.6% $Eu(H_2O)_8^{3+}$. Our results are similar to the X-ray diffraction value of ∼70% $Eu(H_2O)_8^{3+}$ reported by Habenschuss and Spedding, the calculated thermodynamic value of ∼60% reported by Miyakawa, and the trends observed in the neutron diffraction data of Cosy et al. and in the molecular dynamics calculations of Kowall et al.

The current study takes advantage of the symmetry of the $Eu(H_2O)_n$ complexes, and lends further support, from this perspective, that an equilibrium exists between $Eu(H_2O)_8^{3+}$ and $Eu(H_2O)_9^{3+}$, with significant representation from both species.

Acknowledgment. This material is based upon work supported by the National Science Foundation/EPSCoR Grants #EPS-0091948 and #EPS-0082978 and by the State of South Dakota. Kristen Randall was supported through an NSF-REU grant (#CHE-0138951) to the University of South Dakota.

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