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Pressure and Temperature Dependence of the $^7F_0 \rightarrow {}^5D_0$ Excitation Spectrum of Europium(III) as a Probe of the Thermodynamics and Solution Structure of Complexes of Europium(III) with Polyaminocarboxylate Ligands

Christine L. Maupin,[†,‡] Anna Mondry,[§] Leslie Leifer,[†] and James P. Riehl*[,||]

Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931,
Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland, and Department of Chemistry,
University of Minnesota Duluth, Duluth, Minnesota 55812

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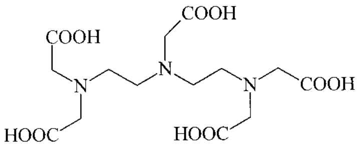
The pressure and temperature dependence of the nondegenerate $^7F_0 \rightarrow {}^5D_0$ excitation spectra of aqueous complexes of Eu(III) with the polyaminocarboxylate ligands triethylenetetraaminehexaacetic acid (ttha) and diethylenetriaminepentaacetic acid (dtpa) have been measured and analyzed in order to probe the solution structure and thermodynamics of these species. The 1:1 metal to ligand complexes of Eu(III) with dtpa show evidence for only one coordination environment for the range of temperatures (5−80 °C) and pressures (1 bar−3 kbar) studied in this work, whereas 1:1 solutions of Eu(III) with dtpa show spectral changes as a function of temperature and pressure which have been interpreted in terms of dimer and monomer structures with different coordination environments. Comparison is made to previous crystallographic results.

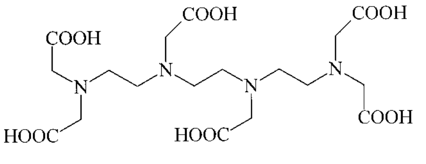
Introduction

Complexes of trivalent and divalent cations with polyaminocarboxylic acid ligands such as diethylenetriaminepentaacetic acid (dtpa = **1**) and triethylenetetra-aminehexaacetic acid (ttha = **2**) and derivatives of these ligands are seeing increased use as probes of biomolecular structure and as radiopharmaceuticals.[1−13] For example, the Gd(III) complex with dtpa is a widely used MRI contrast agent,[1] and the development of other spin probes is an area of active investigation.[2,3] Complexes with the luminescent lanthanide (III) ions, especially Tb(III) and Eu(III), are being used in quantitative biomolecular assays[4−6] and in more qualitative studies of molecular structure.[7] In addition, complexes of ^{111}In,[8−14] ^{153}Sm,[15] ^{88}Y,[12] and ^{99}Tc [16] with this class of multidentate chelating ligand chemically attached to various pharmaceutical substrates are being explored in studies aimed at delivering radioactive species to specific tumor targets. All of these various biological applications exploit the very large stability constant associated with the cation binding to the multidentate polyaminocarboxylate complex, the high solubility of these complexes in aqueous media, and the relatively low toxicity.

The various applications of these complexes do rely upon important specific structural details. The utility of Gd(dtpa)$^{2-}$ as a MRI contrast agent, for example, relies upon the availability of a vacant coordination site involving exchange of water molecules. On the other hand, the luminescence intensity of the complexes of these ligands with lanthanides is quite sensitive to water coordination[17] and, for this reason, some efforts are being made to design complexes in which water molecules have been excluded from the first coordination sphere. The development of radiopharmaceuticals, of course, involves the design and synthesis of complexes with very specific structure:binding characteristics.



H$_5$dtpa (**1**)



H$_6$ttha (**2**)

In this work we concentrate on various spectroscopic studies involving complexes of dtpa and ttha with lanthanide (III) ions. Although the primary interest is in developing useful and reliable spectra−structure relationships for these species in aqueous solution, it is important to connect the spectroscopic results to previously obtained solid-state structures. There have been a number of recent reports of crystal structures of dtpa and ttha complexes with various lanthanide(III) ions. For example, the structure of monomeric dtpa complexes of Nd(III)[18,19] and Gd(III)[1,20] have been reported. They all show a coordination geometry in which the central metal ion is coordinated to 3 nitrogens and 5 oxygens of the ligand with a ninth coordination site occupied by a solvent water molecule. There have also been several reports of dimer structures involving Ln(III) ions with dtpa.[20−22] In these dimer structures the carboxylate connected to one of the terminal nitrogens of each ligand is bound to both Ln(III) ions. Several X-ray structures of crystals containing ttha have also been reported. The larger cations La(III)[23,24] and Nd(III)[25] form monomeric structures with coordination number 10, whereas the smaller ions Yb(III),[26] Dy(III),[23] and Ho(III)[29] exhibit a coordination number of 9. The coordination of these 9 coordinate species consists of 4 nitrogen and 5 oxygen donors.

[†] Michigan Technological University.

[‡] Current address: FDA, HFD-535, Nicholson Research Center, 5600 Fishers Lane, Rockville, MD 20857.

[§] University of Wrocław.

[||] University of Minnesota Duluth.

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Dimeric complexes containing Nd(III)[27]and Gd(III)[28] with a coordination number of 9 (3 nitrogen and 6 oxygen donors) have also been recently reported.

Various type of spectroscopic methods have been applied to the study of the structure of dtpa and ttha and related polyaminocarboxylate complexes with lanthanide (III) ions in solution and in the solid state. These include NMR,[3,30,31] EXAFS,[32] high-resolution absorption spectroscopy,[27,33] and luminescence methods.[7,31,34] In this work we report on the measurement of the temperature and pressure dependence of the nondegenerate $^7F_0 \rightarrow {}^5D_0$ excitation transition of Eu(III) as a probe of the solution structure of complexes with dtpa and ttha. This type of measurement is particularly useful for identifying the presence of multiple solution species, since it is often the case that a single resolvable peak for this transition is observed for each species present. It is shown in this work, for example, that two peaks are observed for 1:1 complexes of Eu(III) with ttha. In addition to these qualitative results, there have been recent examples of quantitative studies involving this technique. For example, Wu and Horrocks[35] have been able to determine stability complexes of many complexes of this type at low pH through H^+ competition studies.

Experimental Section

Excitation of the $^7F_0 \rightarrow {}^5D_0$ transition of Eu(III) (578−582 nm) was accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with a Coherent Innova-70 argon-ion laser as a pump source. The laser dye used in all measurements was Rhodamine 110 dissolved in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser wavelength) was accomplished by passing scattered light from a low-power He−Ne laser through the detection system. The error in the dye-laser wavelength is assumed to equal the resolution of the emission monochromator (0.1 nm). Before and after each excitation scan, the laser intensity was recorded in order to correct for any incident intensity fluctuations. The optical detection system consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emission monochromator was set at 616 nm in order to detect the $^5D_0 \rightarrow {}^7F_2$ emission from Eu(III). The emitted light was detected by a cooled EMI-9558B photomultiplier tube. For temperature-dependent experiments, the temperature of the sample was adjusted and maintained by placing a 1.0 cm cuvette inside an anodized aluminum cuvette jacket which was connected to a Lauda K-4/RD circulating temperature bath. The circulation fluid was a water and ethylene glycol mixture. The connections from the circulator to the aluminum cuvette jacket were insulted with polystyrene to help maintain consistent temperatures. The temperature of the sample was measured by placing a temperature probe (Fisher calibrated to 0.1 °C) directly inside the sample cuvette. The temperature was monitored before and after each luminescence measurement.

Measurements of excitation spectra at greater than atmospheric pressure were accomplished as described previously[36] in a custom-made stainless steel Nova-Swiss high-pressure liquid cell with three sapphire windows. The sample capsule consisted of a modified 10 mm cylindrical glass tube fitted with a Teflon piston with two O-rings. The solution sample is placed into the capsule, which is then placed inside the high-pressure cell block already filled with water which acts as the hydraulic fluid. The high-pressure cell is then pressurized to a fixed static pressure and monitored using a Enerpac hydraulic hand pump and gauge.

Eu(triethylenetetraminehexaacetic acid) Solutions. Triethylenetetraminehexaacetic acid (H_6ttha) was purchased from Aldrich and used without further purification. A stock solution of $Eu(ttha)^{3-}$ was prepared with a pH of approximately 3 by combining the correct weighed proportions of Eu_2O_3 (99.999%), ttha, and guanidine carbonate with water and dissolving over low heat (>60 °C). Aliquots from this stock solution were adjusted to a selected pH by addition of small amounts of guanidine carbonate. The concentration of the final solutions was determined by complexometric titration with EDTA using Xylenol Orange. The final metal:ligand ratio was 1:1.2, and the concentration of the complex was 0.015 M.

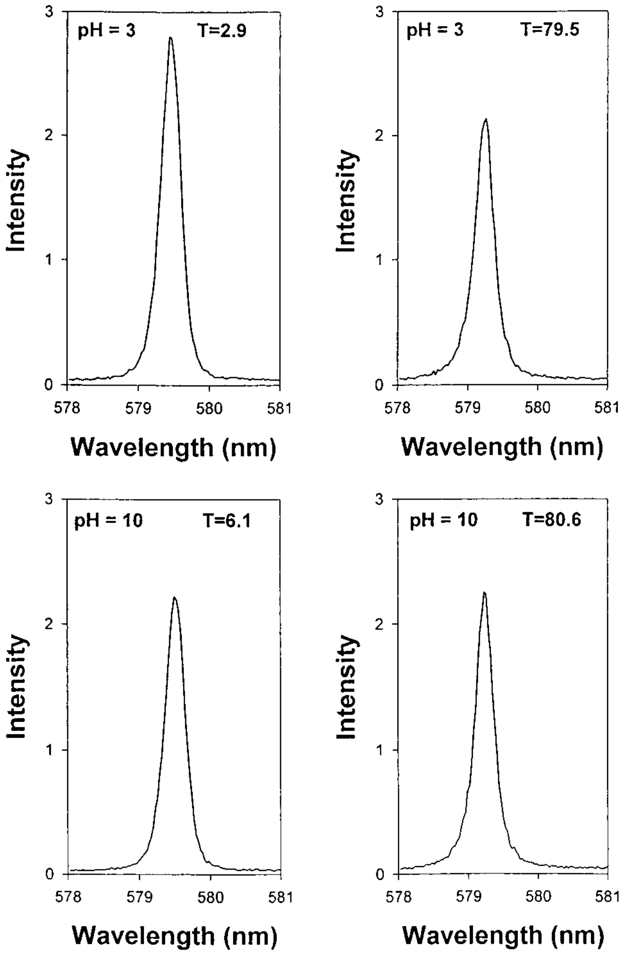

Figure 1. $^7F_0 \rightarrow {}^5D_0$ excitation spectra for an aqueous solution of $Eu(dtpa)^{2-}$ at a metal-to-ligand ratio of 1:1.2 as a function of temperature (°C). Conditions: pH = 10; $\lambda_{em} = 616$ nm.

Eu(diethylenetriaminepentaacetic acid) Solutions. Stock solutions of 0.16 M Eu(III) were prepared by dissolving 99.9% $EuCl_3$ (Aldrich) into D_2O (99.9%) and Milli-Q H_2O. The pH of these solutions was adjusted to between 3 and 3.5 with concentrated HCl. Diethylenetriaminepentaacetic acid (H_5dtpa) was purchased from Aldrich and used without further purification. A stock solution of dtpa was prepared by weighing out the prescribed amount of H_5dtpa and dissolving the sample in Milli-Q water. Solutions were prepared with a ligand-to-metal ratio of 1.2 to 1, and the pH of the final solution was adjusted with concentrated NaOH. The final concentrations of the solutions were determined by complexometric titration with EDTA using Xylenol Orange as an indicator in pH 5.5 acetate buffer to be 0.06 M.

Results

In Figure 1 we plot excitation spectra in the region of the $^7F_0 \rightarrow {}^5D_0$ transition for solutions of Eu(III) and dtpa at two

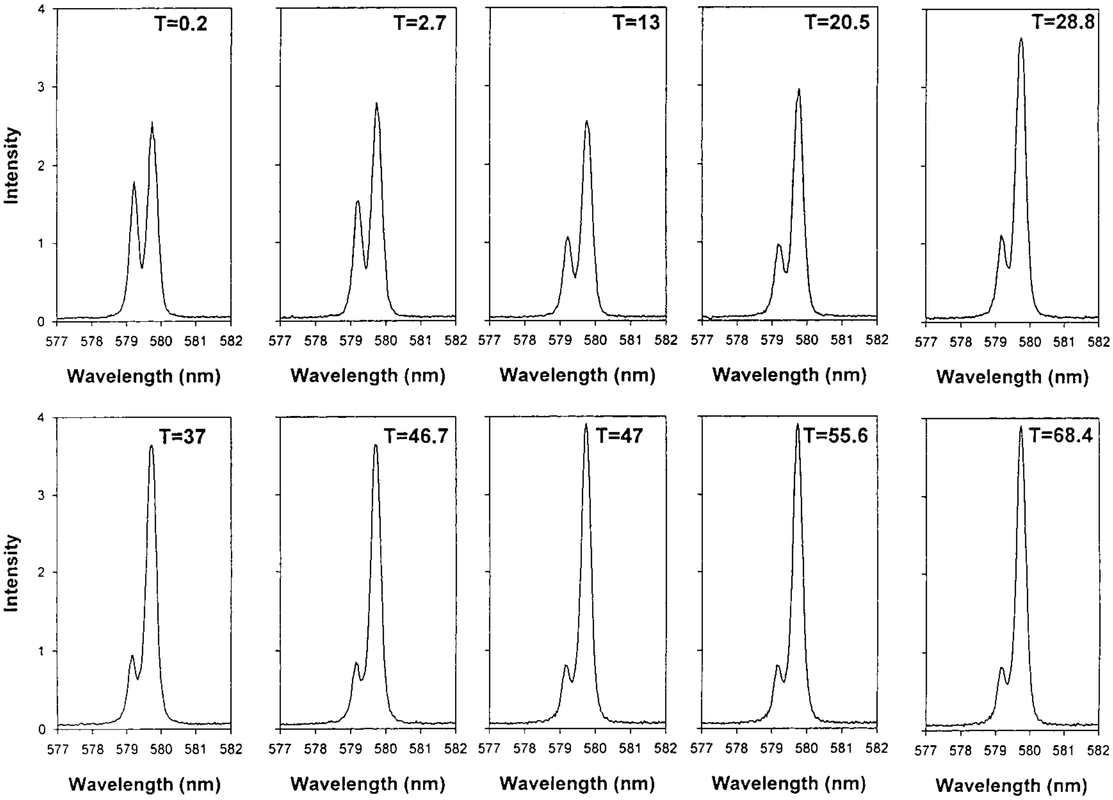

Figure 2. $^7F_0 \rightarrow {}^5D_0$ excitation spectra for an aqueous solution of Eu(ttha)$^{3-}$ at a metal-to-ligand ratio of 1:1.2 at various temperatures (°C). Conditions: pH = 10; $\lambda_{em} = 616$ nm.

different pH values at two different temperatures. As can be seen, there is no measurable shift in the position of the excitation maximum under these various conditions. This is in general agreement with previous results.[33,35] A slight reproducible increase in the luminescence intensity for the low pH solution at low temperature is observed, but a simple interpretation of this result in terms of ligand protonation or other effect is not obvious. In Figure 2 we plot similar spectra for a solution containing Eu(III) and ttha at a pH of 10 as a function of temperature. Note that in this case two peaks are observed and that the relative intensity of the two peaks changes with temperature. Similar results may be obtained at neutral and higher pH values.

In Figure 3 we plot excitation spectra in the region of the $^7F_0 \rightarrow {}^5D_0$ transition for solutions of Eu(III) and ttha as a function of applied hydrostatic pressure. The spectra showed are for a solution at a pH of 10, but similar results are obtained for neutral solutions. In this figure, the effect of pressure on the relative concentration of the two species is easily seen. At room pressure the lower wavelength peak is the more intense, but at the high pressures the relative intensity is reversed.

Theory and Discussion

As seen in Figure 1, the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of solutions of Eu(III) and dtpa under conditions where the metal:dtpa ratio is approximately 1:1 show evidence for the presence of only one species in solution for the range of pH and temperature studied in this work. Previous spectroscopic studies using the method of Horrocks have shown that in aqueous solution the first coordination sphere contains one water molecule.[35,37,38] In addition, the EXAFS results of Benezath et al.[32] have been interpreted in terms of a first coordination sphere containing 5 oxygen and 3 nitrogen donors from the ligand and one oxygen from a coordinated water molecule. All of these spectroscopic results are consistent with the published crystal structure of the lanthanide:dtpa monomers. It should be noted that although this geometry, which is described as a distorted capped square antiprism, should exist in solution as enantiomeric pairs, attempts to measure circularly polarized emission from a photoenriched sample using a circularly polarized excitation source were not successful. This may be due to the fact that the transitions are not strongly chiral or that the enantiomeric pairs are racemizing on a time scale faster than the emission lifetime. It should also be noted that, under conditions in which the metal:ligand ratio is 2:1, Mondry and Riehl[33] have seen evidence for the coexistence of a species in which two Eu(III) ions are bound to a single dtpa molecule.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectra displayed in Figures 2 and 3 for 1:1 solutions of Eu(III) with ttha clearly show the presence of two distinct species. For purposes of discussion, we designate these two species as α and β and identify the β species with the higher wavelength peak. It is assumed that these two species are in rapid equilibrium, so we may write the following expression:

$$\alpha\text{-Eu(ttha)}^{3-} \rightleftarrows \beta\text{-Eu(ttha)}^{3-} \tag{1}$$

Here we have assumed that the ligand carboxylic acids are all deprotonated. As in previous work, we may fit the excitation spectra plotted in Figures 2 and 3 to a sum of two Lorentzian peaks and relate the concentration, *C*, of each species to the corresponding peak area, *A*, as follows:

$$C_\alpha = k_\alpha A_\alpha \quad C_\beta = k_\beta A_\beta \tag{2}$$

The equilibrium constant may then be expressed as

$$K_{eq} = \frac{[\beta\text{-Eu(ttha)}^{3-}]}{[\alpha\text{-Eu(ttha)}^{3-}]} = \frac{k_\beta A_\beta}{k_\alpha A_\alpha} \tag{3}$$

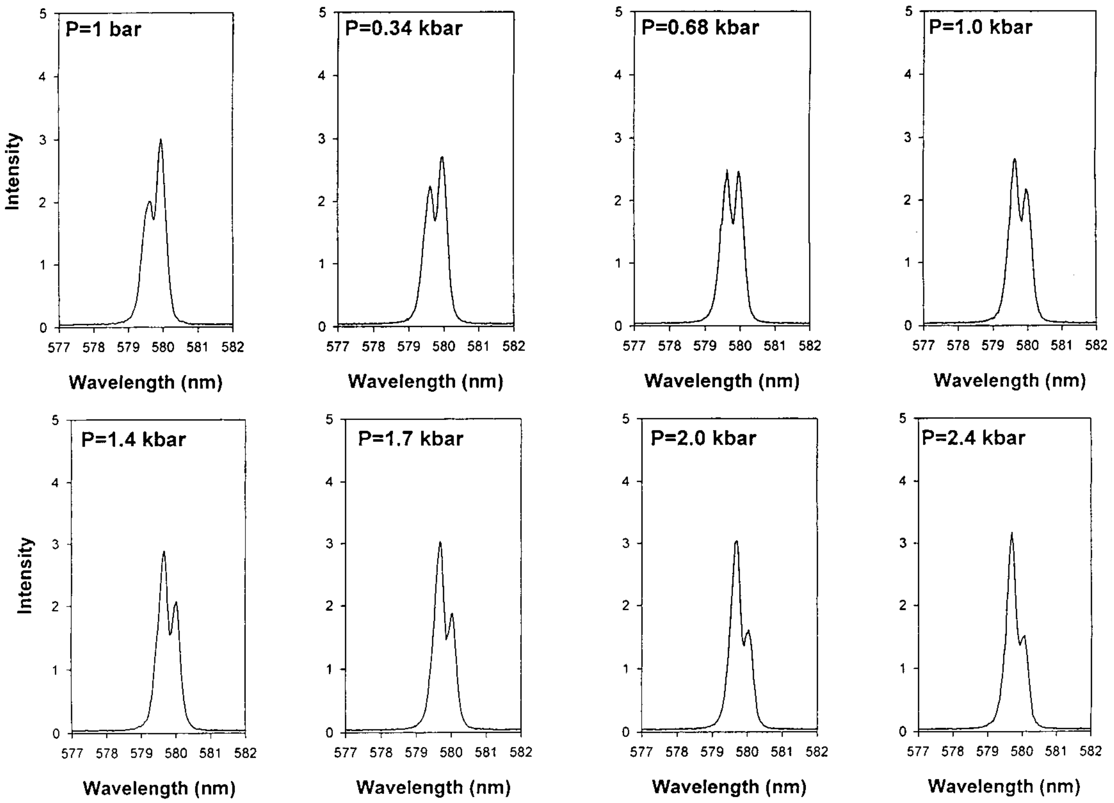

Figure 3. $^7F_0 \rightarrow {}^5D_0$ excitation spectra for an aqueous solution of Eu(ttha)$^{3-}$ at a metal-to-ligand ratio of 1:1.2 at various liquid pressures. Conditions: pH = 10; λ_{em} = 616 nm.

and the temperature dependence of K_{eq} may be related to the enthalpy change as follows:

$$\left(\frac{\partial \ln K_{eq}}{\partial(1/T)}\right)_P = \left(\frac{\partial \ln[A_\beta/A_\alpha]}{\partial(1/T)}\right)_P = -\frac{\Delta H}{R} \tag{4}$$

Here it has been assumed that the proportionality constants k_α and k_β do not depend on temperature. It should be noted that the net concentration of complexes in the $J = 0$ ground state and the $J = 0$ excited state will be affected by changes in the Boltzmann distribution but that the effect will be virtually the same for both species and can be neglected in this analysis. In this case, therefore, one can determine ΔH for the equilibrium reaction from determination of the peak areas without having to determine the individual concentrations of the two species.

In Figure 4 the results from the curve fits of Figure 2 are plotted versus the inverse temperature. The curve fits and subsequent peak areas were obtained using the commercial software package PeakFit from Jandel Scientific. These data have been analyzed by a linear least-squares analysis to obtain ΔH from eq 4 for the equilibrium given in eq 3. The value obtained in this case is +8.8 kJ/mol.

The $^7F_0 \rightarrow {}^5D_0$ excitation spectra displayed in Figure 3 also show that at least two different Eu(III) species are contributing to the broad emission at 613 nm. These results may be analyzed using the same equilibrium as introduced above. The variation of K_{eq} with pressure is given by the following equation:

$$\left(\frac{\partial \ln K_{eq}}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{5}$$

Making the same substitutions as above, we obtain the following

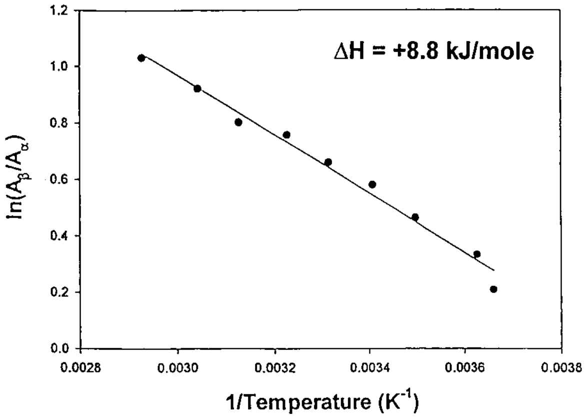

Figure 4. Plot of the natural logarithm of the ratio of Lorentzian peak areas (A_β/A_α) versus inverse temperature for the data presented in Figure 2 for Eu(ttha)$^{3-}$. The solid line is a linear least-squares fit to the data, and ΔH was calculated from eq 4.

expression for the natural logarithm of the equilibrium constant:

$$\ln K_{eq} = \ln\frac{k_\beta}{k_\alpha} + \ln\frac{A_\beta}{A_\alpha} \tag{6}$$

Assuming that the proportionality constants are independent of pressure, we obtain the result

$$\left(\frac{\partial \ln[A_\beta/A_\alpha]}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{7}$$

Increasing pressure does lead to a reduction in solution volume and a resultant increase in concentration, but since this is the same for both species, it has no effect on the overall result presented here. In Figure 5 we plot the logarithm of the ratio

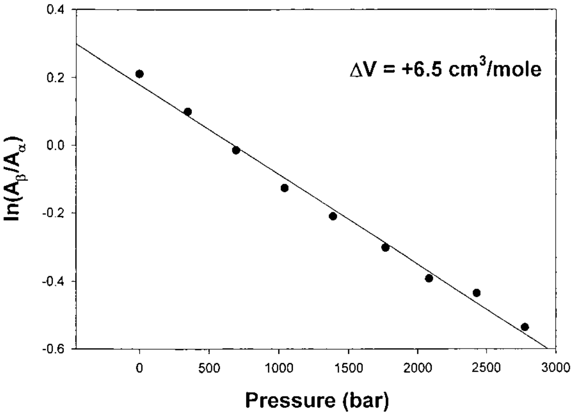

Figure 5. Plot of the natural logarithm of the ratio of Lorentzian peak areas (A_β/A_α) versus pressure P for the data presented in Figure 3 for Eu(ttha)$^{3-}$. The solid line is a linear least-squares fit to the data, and ΔV was calculated from eq 7.

of the peak areas versus P in order to obtain the difference in volume between the two species. A least-squares fit to these data yields a value of 6.5 cm^3/mole for ΔV.

Summary and Conclusions

Although dimer and monomer crystals of dtpa complexes with lanthanides have been found, only one peak is observed in the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum in an aqueous solution of an approximately 1:1 Eu(III):dtpa solution. It is instructive to examine the crystal structures of the Gd(III) complexes of dtpa, since the ionic sizes of these two ions are so similar. In fact, a comparison of the dimer and monomer structure of the Gd(III) complex with this ligand shows that the coordination geometry in these structures are, in fact, very similar. In both structures the coordination environment contains three nitrogen and five oxygen donors from dtpa. In the monomer one of the coordination sites also contains a water molecule, and in the dimer a carboxylate is shared between the two metal ions. The average Gd−O distances are 2.463 Å for the dimer crystal and 2.399 Å for the monomer crystal, and the average Gd−N distances are 2.667 Å for the dimer and 2.694 Å for the monomer. Further indication that the dimer and monomer structures are very similar is given by the density of the two crystals, 1.80 g/cm^3 for the dimer and 1.84 g/cm^3 for the monomer. These data are entirely consistent with the observation that no pressure dependence is seen in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra. Even if there is an equilibrium between dimer and monomer structures in solution, the environments are so similar that they would most likely not be distinguishable by this spectroscopic technique.

A much different situation exists for the 1:1 Eu(III)−ttha solution where two peaks are seen in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra and the intensity of the two peaks changes with pressure and temperature. As pointed out above, dimer and monomer crystals of the Gd(III) have also been studied for this system. A comparison of the internuclear distances shows that the average Gd−O distances (2.40 Å for the dimer crystal and 2.39 Å for the monomer crystal) and the average Gd−N distances (2.68 Å for the dimer and 2.67 Å for the monomer) are almost identical. The difference here is that, in the dimer crystal, the coordination environment contains three nitrogen and six oxygen donors from ttha, whereas in the monomer there are four nitrogen and five oxygen donors. As a result, the local density around the central Gd(III) ion is less in the monomer than in the dimer. An estimate of the volume differences can be obtained from a simple calculation of molecular volume from the crystallographic coordinates. This was accomplished by placing each of the two structures (neglecting hydrogen atoms, solvent molecules, and counterions) in a cubic box, randomly generating points inside the box, and determining whether the point chosen was within the van der Waal radius of any of the constituent atoms. The molecular volume was calculated from the fraction of “hits” multiplied by the volume of the cubic box. For a total of 10^5 points we obtained a molecular volume of the monomer of 383 Å^3, and for the dimer the result was 731 Å^3. The difference in molecular volume per mole (ΔV) is then calculated to be +10 cm^3/mol. Considering the level of approximation used, the neglect of solvent, etc., this is in quite good agreement with the thermodynamic value of +6.45 cm^3/mol. It has been suggested that, depending upon pH and other factors, a monomer with three nitrogen and six oxygen donors from the ttha ligand may coexist with the dimer structure with the same net coordination.[39] This would most likely not be distinguishable in the $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the Eu(III) species, and simple structural models indicate that the density of this complex, if present, would be very similar to the dimer complex discussed above.

From the analysis presented above, we are now able to associate the α complex from the equilibrium defined in eq 1, corresponding to the lower wavelength peak in the $^7F_0 \rightarrow {}^5D_0$ excitation spectrum, with the dimer complex with N_3O_6 coordination, and the β complex with the monomer species involving N_4O_5 coordination. These assignments are not inconsistent with the small positive enthalpy determined for this equilibrium, since the structures of the two complexes are very similar. Since the local charge surrounding the Eu(III) ion is different in the two species, one expects there to be some enthalpy associated with the ligand rearrangements and dimer association. The endothermic result might reflect the fact that the α complex is the lower energy structure because all of the negatively charged carboxylates are coordinated to the central cation, whereas in the β structure one of the carboxylates is not coordinated. It should also be noted that the variation of excitation energy with charge, namely the observation that the species with the higher total charge of coordinated ligands (α) has the lower excitation energy, follows the trend reported by Albin and Horrocks.[39] It has been noted that the use of this trend as a predictive tool should be limited to Eu(III) complexes with very similar ligands.[40]

These results have formed the basis of continuing spectroscopic probes of the solution structure, thermodynamics, and kinetics of multidentate lanthanide complexes in solution. The particular measurements reported here are being applied to other lanthanide systems in which a small number of resolvable $^7F_0 \rightarrow {}^5D_0$ peaks are observed in the excitation spectrum of Eu(III) and which can also be identified with specific complexes.

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