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# ABSORPTION SPECTROSCOPY AS A PROBE OF THE STRUCTURE OF POLYAMINOCARBOXYLATE–Eu(III) COMPLEXES IN SOLUTION

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Absorption spectroscopy was used to study the aqueous solution structure of Eu(III) complexes with DTPA (diethylenetriaminepentaacetic acid) and TTHA (triethylenetetraaminehexaacetic acid). Analysis of the oscillator strengths of the $4f \leftrightarrow 4f$ transitions and of the Judd–Ofelt intensity parameters, $\tau_\lambda$, was performed in order to investigate the formation and the type of bonding in Eu(III)–DTPA and Eu(III)–TTHA species occurring in solution. The correlation of these results with those from other methods made it possible to suggest a relatively complete model of Eu(III)–polyaminocarboxylate coordination.

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## 1. Introduction

Lanthanide complexes with polyaminocarboxylic acid ligands play a considerable role as potential diagnostic agents in magnetic resonance imaging (MRI) [1]. For a better understanding of the structure and dynamics of these multidendate lanthanide(III) complexes in solution, we chose to investigate the Eu(III) complexes with DTPA and TTHA by absorption spectroscopy. These two ligands are higher linear homologues of EDTA.

Absorption spectroscopy measurements for Ln(III) complexes of these ligands are very incomplete [2], although extensive data for Ln(III)–DTPA and TTHA systems are available. NMR [3–5] and luminescence [5, 6] studies of Ln(III)–DTPA chelates in solution are consistent with a single coordinated water molecule and the full coordination potential of the DTPA ligand as found in the X-ray structure of Ba[NdDTPA$\cdot H_2O$]$\cdot 2H_2O$ [7]. The results for Ln(III)–TTHA complexes [5, 8, 9] indicate several different modes of TTHA coordination with light and heavy lanthanide ions.

CPL (circularly polarized luminescence) studies of these two systems performed using circularly polarized excitation show that only a $EuTTHA^{3-}$ complex is chiral and stable on the emission time scale of the Eu(III) ion (1.2 ms) in a wide temperature range (10–80°C) [10].

The aim of our present study was to examine the influence of the coordination of the Eu(III) ion with DTPA and TTHA ligands in aqueous solutions on the Judd–Ofelt parameter values, and on the oscillator strengths of $4f \leftrightarrow 4f$ transitions.

## 2. Experimental

A stock solution of europium perchlorate was prepared from $Eu_2O_3$ (99.9% Merck). The Eu(III) ion concentration was determined complexometrically using xylenol orange as an indicator. Stock solutions of DTPA (98% Aldrich), TTHA (98% Aldrich) and EDTA (98% POCH) were prepared by half neutralization with NaOH. The NaOH solution was also used to adjust the pH of the spectroscopically measured solutions. All spectral measurements were made on a Cary 5 UV-VIS-NIR spectrophotometer at room temperature. Experimental oscillator strength values ($P$) and the Judd–Ofelt intensity parameters, $\tau_\lambda$, were calculated by the method described previously [11]. The accuracy of the very weak absorption bands were checked by performing repeated measurements using different cell path lengths, concentrations, scan rates, etc. Oscillator strengths obtained from repeated measurements varied by only a few percent in the worst cases.

## 3. Results

The absorption spectra of 1:1 metal to ligand Eu(III)–DTPA and TTHA systems were examined over a large pH range (1.67–11.15). It was observed that the transitions $^7F_0 \rightarrow {}^5D_{0,1,2}$ showed the most marked variations in band shape and intensity, and, for this reason, these specific transitions are the primary focus of the work presented here. For example, these transitions displayed a quite different pH dependence during formation of the 1:1 complex for the two systems (see Fig. 1). Above pH = 6.00 no differences were noticed in any of the $4f \leftrightarrow 4f$ transitions in the spectral region 360–650 nm for either Eu(III) complex. Oscillator strengths were determined from measured absorption spectra for the available $4f \leftrightarrow 4f$ transitions, and the results are presented in Table I. In Table II we show oscillator strengths ($P_{\mathrm{corr}}$) corrected for the presence of the thermally excited $^7F_1$ and $^7F_2$ levels. The results given in this table were used to obtain the $\tau_\lambda$ parameters by a numerical fitting procedure [11]. Because of the high similarity in the $^7F_0 \rightarrow {}^5D_0$ band for $EuTTHA^{3-}$ (pH $\geq$ 6.00) and $Eu(EDTA)_2^{5-}$ in alkaline solution (Fig. 1C), oscillator strengths and $\tau_\lambda$ parameters for Eu:EDTA = 1:2 complex (pH = 8.30) are also included in Table II.

The $^7F_0 \rightarrow {}^5D_0$ transition has a relatively high oscillator strength in both investigated systems. Two components of the $^7F_0 \rightarrow {}^5D_0$ transition (579.00 nm

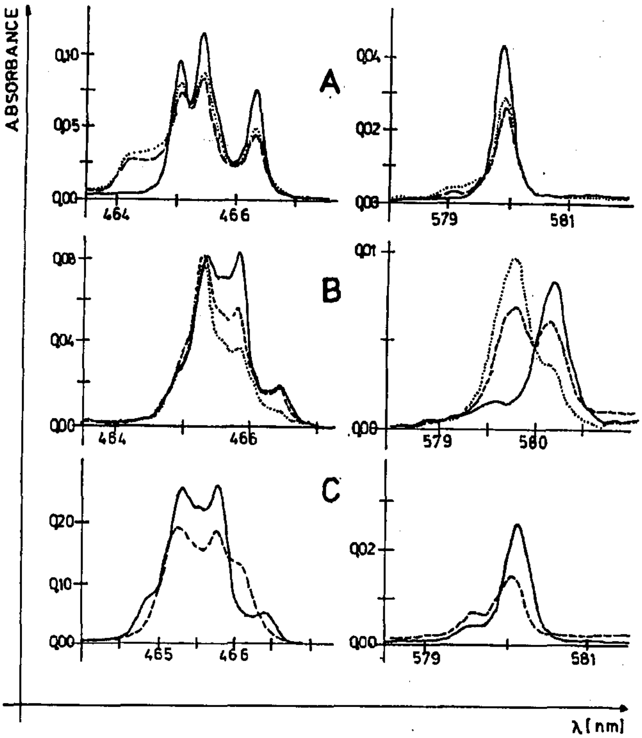

Fig. 1. Effect of pH on the $^7F_0 \rightarrow {}^5D_2$ and $^7F_0 \rightarrow {}^5D_0$ transitions in the absorption spectrum of Eu(III) ion for: (A) EuDTPA$^{2-}$: $c_{\mathrm{Eu}^{3+}} = 0.08164$ M, $c_{\mathrm{DTPA}^{5-}} = 0.0945$ M, $l = 4$ cm, - - - - - - pH = 1.67, ········ pH = 5.67, —— pH = 7.81; (B) EuTTHA$^{3-}$: $c_{\mathrm{Eu}^{3+}} = 0.05132$ M, $c_{\mathrm{TTHA}^{6-}} = 0.0601$ M, $l = 2$ cm, ········ pH = 2.39, - - - - - - pH = 4.16, —— pH = 6.33; (C) —— EuTTHA$^{3-}$, pH = 8.06, $c_{\mathrm{Eu}^{3+}} = 0.08164$ M, $c_{\mathrm{TTHA}^{6-}} = 0.0945$ M, $l = 4$ cm - - - - - - Eu(EDTA)$_2^{5-}$, pH = 8.30, $c_{\mathrm{Eu}^{3+}} = 0.05481$ M, $c_{\mathrm{EDTA}^{4-}} = 0.1120$ M, $l = 4$ cm.

and 579.86 nm) for EuDTPA$^{2-}$ are observed at low pH values, while at pH above 6.00 only one component at 579.86 nm is detected (Fig. 1A). For the EuTTHA$^{3-}$ complex two components of the $^7F_0 \rightarrow {}^5D_0$ transition are seen throughout the whole pH range. The relative intensity of the two components depends on the pH of the solution (Fig. 1B). The maximum of the first component shifts depending on pH, whereas the second peak (580.16 nm) is pH independent. A different pattern of intensity changes with increase in pH is observed for EuDTPA$^{2-}$ (pH = 1.67, $P = 0.55 \times 10^{-8}$; pH = 7.81, $P = 0.84 \times 10^{-8}$), as compared to EuTTHA$^{3-}$ (pH = 2.39, $P = 0.69 \times 10^{-8}$; pH $\geq$ 6.33, $P = 0.51 \times 10^{-8}$).

The intensity of the $^7F_0 \rightarrow {}^5D_1$ transition was the same for all investigated solutions ($P = 1.59 \times 10^{-8}$), however, the shape of bands do change. This observation is consistent with the magnetic dipole character of this transition, and, as such, serves as a useful reference point for the other intensity measurements.

TABLE I

Experimental oscillator strength values ($P_{\text{exp}}$) and the gravity centers of bands for $\text{EuDTPA}^{2-}$ (pH = 7.84) and $\text{EuTTHA}^{3-}$ (pH = 6.46). $c_{\text{Eu}^{3+}} = 0.08164$ M.

| | $\text{EuDTPA}^{2-}$ | | $\text{EuTTHA}^{3-}$ | |
|---|---|---|---|---|
| | $E$ [cm$^{-1}$] | $P_{\text{exp}} \times 10^8$ | $E$ [cm$^{-1}$] | $P_{\text{exp}} \times 10^8$ |
| $^7F_0 \rightarrow {}^5D_4$ | 27573 | 31.00 | 27568 | 38.10 |
| $^7F_1 \rightarrow {}^5D_4$ | 27278 | 6.86 | 27275 | 6.56 |
| $^7F_0 \rightarrow {}^5G_{6,5,4,3}$ | 26553 | 65.68 | 26594 | 55.49 |
| $^7F_0 \rightarrow {}^5G_2$ | 26272 | 38.88 | 26244 | 46.10 |
| $^7F_1 \rightarrow {}^5G_2$ | 25984 | 43.30 | 25924 | 37.58 |
| $^7F_0 \rightarrow {}^5L_6$ | 25333 | 236.86 | 25313 | 242.50 |
| $^7F_1 \rightarrow {}^5L_6$ | 25053 | 41.23 | 25019 | 44.48 |
| $^7F_1 \rightarrow {}^5D_3$ | 23914 | 5.18 | 24047 | 7.55 |
| $^7F_0 \rightarrow {}^5D_2$ | 21488 | 6.98 | 21469 | 15.72 |
| $^7F_1 \rightarrow {}^5D_2$ | 21198 | 0.44 | 21164 | 0.84 |
| $^7F_2 \rightarrow {}^5D_2$ | 20483 | – | 20488 | 0.80 |
| $^7F_0 \rightarrow {}^5D_1$ | 18986 | 1.59 | 18981 | 1.59 |
| $^7F_1 \rightarrow {}^5D_1$ | 18707 | 2.71 | 18693 | 6.05 |
| $^7F_2 \rightarrow {}^5D_1$ | – | – | 18013 | 0.40 |
| $^7F_0 \rightarrow {}^5D_0$ | 17246 | 0.84 | 17237 | 0.51 |
| $^7F_1 \rightarrow {}^5D_0$ | 16966 | 1.93 | 16941 | 1.37 |
| $^7F_2 \rightarrow {}^5D_0$ | – | – | 16275 | 0.37 |

The oscillator strength ($P$) of the "hypersensitive" $^7F_0 \rightarrow {}^5D_2$ transition for $\text{EuDTPA}^{2-}$ in the whole pH range remains almost constant (pH = 1.67, $P = 6.24 \times 10^{-8}$; pH = 7.81, $P = 6.98 \times 10^{-8}$), while for the $\text{EuTTHA}^{3-}$ complex a significant increase in $P$ is observed (pH = 2.39, $P = 11.92 \times 10^{-8}$; pH $\geq$ 6.33, $P = 15.72 \times 10^{-8}$).

## 4. Discussion

Among all the $4f \leftrightarrow 4f$ transitions, the so-called "hypersensitive" transitions of lanthanide ions are the most sensitive to changes in the immediate environment of the metal ion. On the other hand, the Judd–Ofelt intensity parameters, $\tau_\lambda$, often give a better insight into interpretation of the entire spectrum, because in many cases intensity changes are not limited to the "hypersensitive" transitions only. The results collected in Table II clearly indicate that for all analyzed spectra only the $\tau_2$ parameter values change significantly, whereas $\tau_4$ and $\tau_6$ values remain constant within the limit of experimental error. The large relative errors associated

TABLE II

Oscillator strength values calculated from the $^7F_0$ state with regard to the correction for population of the $^7F_1$ and $^7F_2$ states ($P_{\mathrm{corr}}$), oscillator strength values calculated from the Judd–Ofelt theory ($P_{\mathrm{calc}}$) and the Judd–Ofelt parameter values $\tau_\lambda$ for EuDTPA$^{2-}$, EuTTHA$^{3-}$ and Eu(EDTA)$_2^{5-}$. EuDTPA$^{2-}$: $c_{\mathrm{Eu^{3+}}} = 0.08164$ M, $c_{\mathrm{DTPA^{5-}}} = 0.0945$ M, pH = 7.81. EuTTHA$^{3-}$: $c_{\mathrm{Eu^{3+}}} = 0.08164$ M, $c_{\mathrm{TTHA^{6-}}} = 0.0945$ M, pH = 6.46. Eu(EDTA)$_2^{5-}$: $c_{\mathrm{Eu^{3+}}} = 0.05481$ M, $c_{\mathrm{EDTA^{4-}}} = 0.1120$ M, pH = 8.30.

| | EuDTPA$^{2-}$ | | EuTTHA$^{3-}$ | | Eu(EDTA)$_2^{5-}$ | |
|---|---|---|---|---|---|---|
| | $P_{\mathrm{corr}}$ $\times 10^8$ | $P_{\mathrm{calc}}$ $\times 10^8$ | $P_{\mathrm{corr}}$ $\times 10^8$ | $P_{\mathrm{calc}}$ $\times 10^8$ | $P_{\mathrm{corr}}$ $\times 10^8$ | $P_{\mathrm{calc}}$ $\times 10^8$ |
| $^7F_0 \rightarrow {}^5D_4$ | 41.05 | 33.07 | 49.75 | 32.91 | 46.25 | 28.86 |
| $^7F_0 \rightarrow {}^5G_{6,5,4,3}$ | 86.97 | 100.00 | 72.46 | 99.88 | 78.21 | 106.58 |
| $^7F_0 \rightarrow {}^5L_6$ | 313.64 | 310.30 | 316.64 | 309.29 | 352.57 | 345.27 |
| $^7F_0 \rightarrow {}^5D_2$ | 9.24 | 9.24 | 20.53 | 20.53 | 20.06 | 20.06 |
| $^7F_0 \rightarrow {}^5D_1$ | 2.11 | 0.00 | 2.08 | 0.00 | 2.10 | 0.00 |
| $\tau_2 \times 10^9$ | $5.38 \pm 6.49$ | | $11.95 \pm 13.85$ | | $11.67 \pm 14.04$ | |
| $\tau_4 \times 10^9$ | $10.90 \pm 3.16$ | | $10.86 \pm 6.62$ | | $9.51 \pm 6.84$ | |
| $\tau_6 \times 10^9$ | $7.90 \pm 0.28$ | | $7.88 \pm 0.58$ | | $7.98 \pm 0.60$ | |

with the $\tau_2$ parameters are due to the limited number of transitions used in the fitting procedure, and to the fact that the transitions are quite weak. Errors of this magnitude are common in Eu(III) parametrization in this type of analysis for aqueous solution studies.

Oscillator strengths of "hypersensitive" transitions may be used to probe the coordination environment of lanthanide complexes in solution. The oscillator strength of the $^7F_0 \rightarrow {}^5D_2$ transition for EuDTPA$^{2-}$ is much smaller than that for EuTTHA$^{3-}$ and does not undergo significant intensity changes even at low pH values where the coexistence of 2:1 and 1:1 metal to ligand species (as evidenced by the $^7F_0 \rightarrow {}^5D_0$ transition) are observed (Fig. 1A). The very small changes in oscillator strengths of the $^7F_0 \rightarrow {}^5D_2$ transition suggest that the nearest neighbor environment of the Eu(III) ion does not change significantly.

A much more complex situation exists in the Eu(III)–TTHA system. At low pH values the presence of 2:1 and 1:1 species are shown by the existence of two different excited state lifetimes, while at pH above 6.00 two components of the $^7F_0 \rightarrow {}^5D_0$ transition have only one emission lifetime [9]. This latter observation suggests the presence of two distinct 1:1 species for Eu(TTHA)$^{3-}$ under these conditions. This explains very well the large difference in intensities of the "hypersensitive" $^7F_0 \rightarrow {}^5D_2$ transition (as well as in $\tau_2$ values) between the Eu(III)–DTPA and TTHA systems. The oscillator strength of the $^7F_0 \rightarrow {}^5D_2$ transition and $\tau_2$ for the $EuTTHA^{3-}$ complex are comparable with those obtained for Eu(III)–EDTA. This latter system has also been shown to be composed of different types of 1:1 and 1:2 metal to ligand complexes [12].

The results presented above indicate that high resolution sensitive absorption measurements of this type may be used to obtain specific information concerning details of lanthanide ion binding, including the existence of multiple species in aqueous solutions. Conclusions concerning the specific solution structure of $EuDTPA^{2-}$ and $EuTTHA^{3-}$ have been presented, based on the determination of oscillator strengths and the Judd–Ofelt intensity parameters. The results obtained here are in general agreement with previous work on the coordination environment of polyaminocarboxylate lanthanide complexes, and should serve as a basis for continuing work in this area.

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