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Applications of lanthanide luminescence spectroscopy to solution studies of coordination chemistry

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Contents

Abstract

Luminescence spectroscopy is an important technique for the study of the coordination chemistry of the lanthanide ions in both the solution and solid state. This article concentrates on applications aimed at elucidating the coordination structure in solution phase systems. Luminescence lifetime measurements which allow the examination of the metal ion coordination environment in a wide variety of ligand systems are discussed. In addition, recent developments in the use of Eu(III) $^7F_0 \rightarrow ^5D_0$ excitation spectroscopy are presented. In the final section, the application of luminescence techniques to the examination of ligand sensitized lanthanide luminescence is reviewed briefly. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Optical spectroscopy is an important tool for the study of coordination chemistry of Ln(III) ions in solution, as attested to by the many reviews of the application of either absorption or luminescence spectroscopy to such research. Some excellent examples are the reviews of Yatsimirskii and Davidenko [1], Richardson [2], and Horrocks and Albin [3]. Valuable reviews concerning the photophysical aspects of lanthanide spectroscopy are also available [4,5]. The importance of gadolinium chelates as contrast agents for magnetic resonance imaging [6], and the use of lanthanide chelates as sensitive bioanalytical assays [7], and in other applications, have been reviewed by a number of authors. Examples are the reviews of Parker and Williams [8] and Sabbatini et al. [9]. In this article, we describe some recent applications of lanthanide luminescence to the study of lanthanide complexation chemistry in solution.

Particular emphasis in this review is placed on the use of the luminescence lifetimes of aquated Eu(III) and Tb(III) ions in H_2O solutions to determine the number of water molecules coordinated in the inner sphere of Ln(III) ions bound in complexes. The utility of excitation spectroscopy of the Eu(III) $^5D_0 \rightarrow {}^7F_0$ band to the study of the coordination environment of the Eu(III) ion is also discussed. A third emphasis is ligand sensitized lanthanide luminescence. Such sensitized emission occurs when an organic ligand, which is coordinated to the metal ion, absorbs UV or near-UV radiation and subsequently transfers this energy to the Ln(III) ion which subsequently emits the energy via luminescence. This ligand sensitized lanthanide luminescence has been employed in the development of ultrasensitive bioassays [7,10,11].

2. Lanthanide spectroscopy

The lanthanide series, comprised of the 14 elements (atomic numbers 58–71) which follow lanthanum in the Periodic Table, is characterized by successive filling of the 4f orbitals. Due to the shielding of the 4f orbitals by the outer lying $5s^25p^6$ filled subshells of the xenon configuration, the spectral properties of Ln(III) ions are minimally perturbed by the external field generated by ligands or counter anion molecules. This results in very narrow f→f absorption bands compared to the broad d→d absorption bands of d-block transition metals. The transitions between the $4f^n$ configurations of the Ln(III) ions are "Laporte forbidden" (there is no change of parity from the ground state to the excited state). Therefore, these transitions are weak in both absorption and emission, having molar absorptivities generally less than $10\ M^{-1}\ cm^{-1}$ and radiative lifetimes in the range of 0.1–>1.0 ms. The absorption and emission characteristics of the trivalent lanthanides differ strikingly from those of organic chromophores, for which molar absorptivities $>10^4\ M^{-1}\ cm^{-1}$ and radiative lifetimes in the nanosecond range are common.

While the f→f transitions of the lanthanides are generally insensitive to the ligand field surrounding the metal ion, some transitions show intensity variations which depend upon the chemical environment. These transitions are referred to as hypersensitive transitions and generally follow the selection rules $|\Delta J| \leqslant 2$ and $|\Delta L| \leqslant 2$. Some typical examples of this type of transition are $^4I_{9/2} \rightarrow {}^4G_{5/2}$ for Nd(III), $^6H_{5/2} \rightarrow {}^6F_{4/2}$ for Sm(III), $^7F_2 \rightarrow {}^5D_0$ for Eu(III), $^6H_{15/2} \rightarrow {}^6F_{11/2}$ for Dy(III), and $^3H_6 \rightarrow {}^3F_4$ for Tm(III). Because the intensity and in some cases the peak maxima of these hypersensitive transitions show strong dependencies upon the Ln(III) ion environment, these transitions can be used to probe aspects of the coordination structure of the Ln(III) ion.

Anhydrous salts of the lanthanides are known to exhibit luminescence which is exploited in their use as solid state laser materials or phosphors for color television screens. By contrast, hydrated crystals of the lanthanides exhibit much lower luminescence intensity for the members in the center of the series (Sm, Eu, Gd, Tb, Dy) and essentially no luminescence at the beginning or end of the series. The predominant luminescence transitions for the lanthanide ions that exhibit luminescence as aquated ions and the lifetime of the lowest energy emitting state are given in Table 1.

The weak luminescence of the aquated Ln(III) ions indicates that the high energy vibrations of O–H groups present in the crystal lattice provide an efficient mechanism for the non-radiative de-excitation of the Ln(III) excited states. Kropp and Windsor [12,13] studied the luminescence intensity and lifetimes of Eu(III) and Tb(III) compounds in H_2O and D_2O solutions and observed greater intensities and longer-lived luminescence of the Ln(III) ions in the D_2O solutions. In addition, they pointed out that the ratio of the fluorescence intensity from a Ln(III) excited state in D_2O solution to the intensity observed in H_2O solution is inversely proportional to the energy gap between the Ln(III) ion luminescent state and the ground state manifold. Haas and Stein [14] demonstrated that the observed luminescence decay constant for the $^5D_0$ excited state of Eu(III) in mixtures of water and acetonitrile is proportional to the number of water molecules in the primary coordination sphere of the ion. They also proposed that each water molecule quenches the excited state population independently.

Stein and Würzberg [15] concluded that the energy gap between the emissive state and the highest lying sublevel of the ground state of Eu(III) or Tb(III) could be effectively spanned by the vibrational modes of hydroxyl oscillators coordinated to

Table 1
Predominant luminescence transitions for some lanthanide ions and their lifetimes as aquated ions in aqueous solution

Lanthanide	Transition	Wavelength (nm)	Lifetime (ms)
Sm	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	594	0.0023
Eu	$^5D_0 \rightarrow {}^7F_2$	616	0.11
Gd	$^6P_{7/2} \rightarrow {}^7S_{7/2}$	310	2.3
Tb	$^5D_4 \rightarrow {}^7F_5$	543	0.4
Dy	$^4F_{9/2} \rightarrow {}^6H_{15/2}$	479	0.0024

the metal center. A partial energy diagram of the Eu(III) and Tb(III) energy levels and the O–H ($\nu_{sym} = 3700\ cm^{-1}$) and O–D ($\nu_{sym} = 2600\ cm^{-1}$) vibrational overtones of coordinated water molecules is presented in Fig. 1. As shown in Fig. 1, the energy gap between the luminescent state and ground state manifold is approximately 12 000 cm^{-1} for Eu(III) while that of Tb(III) is approximately 15 000 cm^{-1}. The coupling of the Ln(III) excited states to the vibrational overtones of coordinated O–H oscillators provides an efficient mechanism for energy transfer, resulting in radiationless de-excitation of the Ln(III) ion excited state. Coupling to a higher energy overtone, as required for the O–D oscillator, results in less efficient quenching of the Ln(III) excited state, and longer-lived Ln(III) luminescence.

A particularly useful feature of the Eu(III) ion is the excitation spectra of the $^7F_0 \rightarrow {^5D_0}$ transition. Both the ground state and the excited state are non-degenerate, which results in each distinct Eu(III) environment exhibiting a singlet peak in the excitation spectrum. However, the 0–0 band is extremely weak because it is forbidden by electronic selection rules. Furthermore, when the Eu(III) ion is in a high symmetry environment or a center of inversion is present, the 0–0 transition is also forbidden by symmetry selection rules. The weak intensity in asymmetric environments normally requires laser excitation techniques to provide sufficient intensities to observe the Eu(III) $^7F_0 \rightarrow {^5D_0}$ transition.

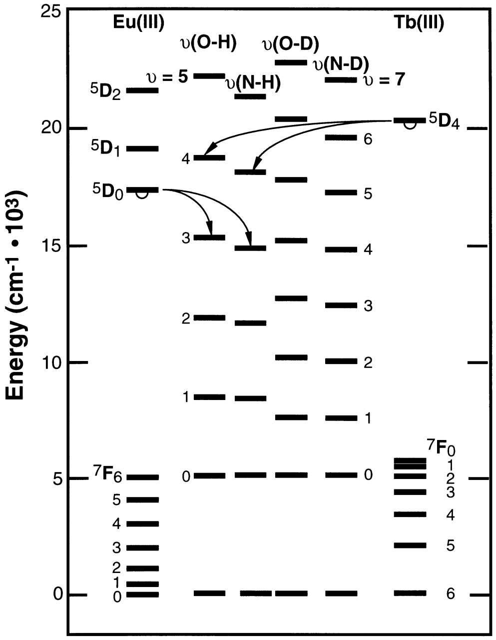


Fig. 1. Energy diagram of Eu(III) and Tb(III) and the vibrational energy levels of O–H, O–D, amine N–H, amine N–D oscillators. Semi-circles denote the lowest luminescent levels. Curved arrows denote the most likely vibrational overtone for the non-radiative decay processes.

3. Lanthanide luminescence lifetime measurements

3.1. Determination of primary hydration number

The use of luminescence lifetime measurements to determine the number of water molecules bound in the primary coordination sphere of the lanthanide ion has been the object of a growing number of studies. Following the work of Haas and Stein [14] and Stein and Würzberg [15], Horrocks and Sudnick [16,17] developed a quantitative expression for the number of water molecules coordinated in the inner sphere of the Ln(III) ion. From the linear relationship of the observed luminescence decay constants of a series of crystalline Eu(III) and Tb(III) hydrated and deuterated complexes with the known number of coordinated water molecules in these solid hydrates, these researchers derived Eq. (1), where n is the number of water molecules in the inner sphere of the Ln(III) ion, $A_{\mathrm{Eu}}=1.05$, $A_{\mathrm{Tb}}=4.2$, and the values of τ^{-1} are in inverse milliseconds.

$$n=A_{\mathrm{Ln}}(\tau^{-1}_{\mathrm{H_2O}}-\tau^{-1}_{\mathrm{D_2O}}) \tag{1}$$

Depending upon the accuracy of the determined Ln(III) luminescence decay constants, the range of uncertainty of the Eu(III) or Tb(III) hydration numbers calculated using Eq. (1) is ±0.2 to ±0.5 water molecules.

Barthelemy and Choppin [18] determined the luminescence decay constants for a variety of crystalline Eu(III) complexes of carboxylate and sulfate ligands of known hydration number, grown in H_2O and D_2O solution, respectively. Assuming there was no contribution from the ligand to the de-excitation of the Eu(III) excited state, the authors developed a relationship between the hydration number of the Eu(III) ion in the various complexes using only the luminescence decay constant obtained in H_2O solution. The equation is:

$$n=1.05\times\tau^{-1}_{\mathrm{H_2O}}-0.70 \tag{2}$$

The authors demonstrated that Eu(III) hydration numbers calculated using this simpler relationship were consistent within experimental uncertainty with values obtained using the equation derived by Horrocks and Sudnick [16,17]. In cases of ligands which possess moieties with high energy vibrations, the assumption that the ligand does not contribute to the quenching of the Eu(III) excited state can limit the applicability of this equation. However, in general, ligands are not as effective at promoting the radiationless de-excitation of Ln(III) excited states as the O–H oscillator of inner sphere coordinated water molecules [3,19,20].

3.2. Determination of other donor numbers

The high energy vibrations of coordinated groups other than the O–H moiety may also quench excited states of Ln(III) ions. The N–H ($\nu_{\mathrm{sym}}=3300\ \mathrm{cm}^{-1}$) or C–H ($\nu_{\mathrm{sym}}=2900\ \mathrm{cm}^{-1}$) groups of coordinated ligands quench the excited state in a manner similar to that of coordinated water molecules. The energy of the N–H vibrational overtones in relation to the luminescent Eu(III) and Tb(III) excited states is shown in Fig. 1. Wang et al. [21] determined the luminescence lifetimes of Eu(III) and Tb(III) ethylenediamine complexes in DMSO. The ethylenediamine ligand contains four N–H groups and these N–H groups coordinate Eu(III) or Tb(III) ions and efficiently quench the Ln(III) excited states. The quenching of the Eu(III) and Tb(III) luminescence is linearly proportional to the number of N–H groups in the inner coordination sphere of the metal. The authors derived the following quantitative relationships for the observed luminescence decay rate constants as a function of the number of N–H groups bound to the metal ions for Eu(III) [Eq. (3)] and for Tb(III) [Eq. (4)], respectively:

$$k_{\mathrm{obs}} = (7.6 \times 10^{-1} \pm 2.3 \times 10^{-2}) n_{\mathrm{N\text{–}H}} + (4.2 \times 10^{-1} \pm 1.9 \times 10^{-2}) \qquad (3)$$

$$k_{\mathrm{obs}} = (7.3 \times 10^{-2} \pm 3.2 \times 10^{-3}) n_{\mathrm{N\text{–}H}} + (3.0 \times 10^{-1} \pm 2.7 \times 10^{-2}) \qquad (4)$$

The authors concluded that the extent of quenching of the Ln(III) excited state by a coordinated N–H oscillator is 150% of the O–H oscillator for Eu(III) and 52% for Tb(III).

Previous work [22,23] has demonstrated that the Eu(III) complexes of 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetate (DOTA) contain approximately one inner sphere coordinated water molecule. Anelli et al. [24] and Dickins et al. [25] have examined the luminescence lifetimes of europium complexes of substituted-DOTA derivatives which had N–H or C–H moieties coordinated to the metal. Anelli et al. [24] concluded that the N–H oscillator was nearly as efficient as the O–H oscillator in terms of promoting the radiationless decay of excited state Eu(III). Dickins et al. [25] proposed that, in addition to the contributions of inner sphere coordinated C–H, N–H, or O–H oscillators, the quenching of O–H oscillators near, i.e. in the outer coordination sphere, must be considered in order to explain fractional hydration numbers.

In addition to other techniques, Di Bernardo et al. [26] used luminescence lifetime measurements to characterize the Ln(III) complexation of the branched amine tris(2-aminoethyl)amine (tren) and the linear amine tetraethylenepentaamine (tetren) in dimethyl sulfoxide solution. The luminescence lifetime data for the Eu(III) and Tb(III) complexes of tren indicated that approximately 10 N–H oscillators (five NH_2 groups) interact with the metal center in the 1:2 tren complexes. Since each tren molecule has three NH_2 groups, the coordination number predicted from the luminescence measurements, $CN_I = 5$, agreed well with predictions based upon thermodynamic measurements. In the case of the 1:2 tetren complexes, a value of $CN_I = 7$ was calculated from the Eu(III) and Tb(III) luminescence lifetime data. The authors concluded that two NH_2 and five N–H groups were involved in the binding of Ln(III) cations by the tetren ligand.

3.3. Examination of inner sphere versus outer sphere complexation

The above relationships have been applied to the study of the primary coordination sphere of lanthanide ions in solution. An important question of lanthanide coordination chemistry is whether a metal–ligand complex involves inner or outer sphere interaction. Formation of an inner sphere complex causes a decrease in the number of water molecules coordinated to the Ln(III) ion, while formation of an outer sphere complex leaves the primary coordination sphere intact. Unfortunately, studies of a particular ligand system using various methods such as thermodynamic, UV–vis, or NMR measurements often predict differing extents of inner versus outer sphere complexation [27]. Luminescence lifetimes provide a direct measure of the composition of the inner coordination sphere of Ln(III) complexes with inorganic and organic ligands.

Complexation of lanthanides by the chloride anion in aqueous solution has been examined using lanthanide luminescence spectroscopy [28,29]. The variation in the values of the Eu(III) and Tb(III) hydration numbers with increasing HCl concentration was consistent with outer sphere complexation ($EuCl_n$, $n=1$, 2) to approximately 5 M HCl. For the perchlorate anion, which is generally considered a strictly outer sphere ligand, an “anomalous” increase in the Eu(III) hydration number (from ca. 8 to 9) with increasing anion concentration has been reported [30–33]. This increase could be due to increased quenching of the Eu(III) luminescence by increased hydration as the perchlorate anion concentration increased. However, Lis and Choppin [28] argued that a better interpretation involved an essentially constant primary hydration number with the enhanced quenching due to stronger interaction of the Ln(III) ion with the OH oscillators already present in the inner coordination sphere. This stronger metal–primary sphere water interaction results from the decrease in secondary sphere hydration by the increased H^+ or ClO_4^- ion concentrations.

The relative extent of inner versus outer sphere complexation of Ln(III) ions by acetate and chloroacetates has been estimated from La-139 NMR spectroscopy [34], entropies of complexation [27], and lanthanide luminescence lifetime measurements [35]. The percentages of inner sphere complex formation, determined with the different techniques, are listed in Table 2. As the data in Table 2 shows, the three techniques give similar estimates for the degree of inner sphere complexation for the Ln(III)–acetate and Ln(III)–chloroacetates with the extent of inner sphere complexation increasing with ligand basicity.

Table 2
Nature of complexation of $(EuCl_nCH_{3-n}CO_2)^{2+}$ [a]

	% Inner sphere		
Complex	Luminescence	Thermodynamics	NMR
$EuAc^{2+}$	100	100	100
$EuClAc^{2+}$	100	100	50
$EuCl_2Ac^{2+}$	50	50	25
$EuCl_3Ac^{2+}$	0	10	0

[a] Adapted from ref. [27].

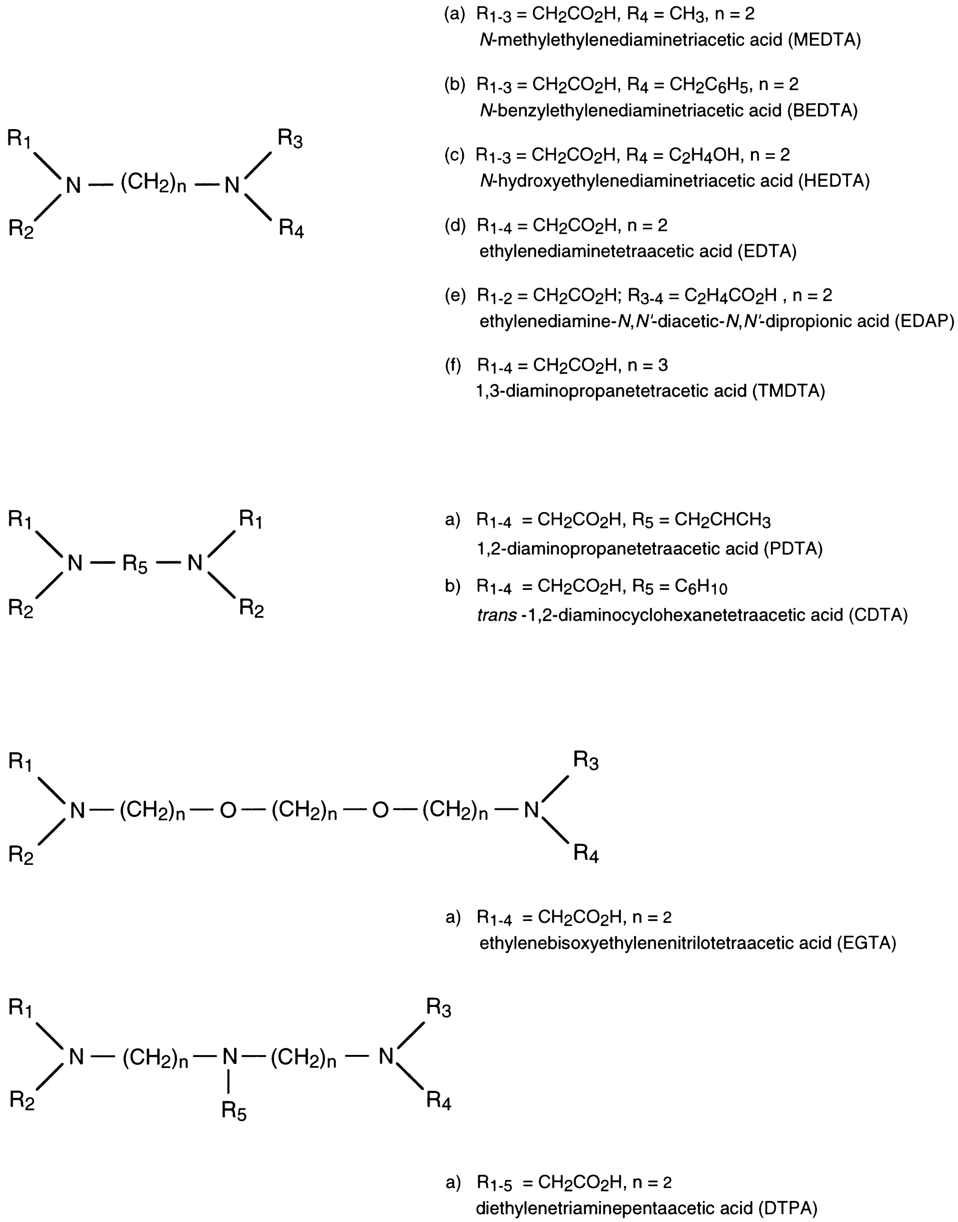
3.4. Hydration numbers in lanthanide polyaminopolycarboxylate complexes

Since the first use of polyaminopolycarboxylate ligands in the ion exchange separation of the lanthanide elements, the study of lanthanide complexation by this class of ligands has been a major area of interest [36]. Lanthanide luminescence has been used to determine the residual hydration numbers of bound Eu(III) or Tb(III) ions and, by implication, to estimate the number of coordinated donors of the ligand. Brittain et al. [37] used luminescence lifetime measurements to determine the hydration state of the Eu(III) and Tb(III) ions in their complexes with a series of polyaminopolycarboxylate ligands (see Scheme 1 for ligand structures). The hydration numbers, *n*, were determined for the 1:1 complexes as a function of solution pH. For all ligand systems studied, the Eu(III) or Tb(III) hydration numbers decreased as the solution pH was increased from pH 1.5 to approximately 3.5. Stable hydration numbers were determined, in the range of pH 4–8, for all the complexes examined. The reported trend in observed Ln(III) hydration numbers with increasing pH was similar for the analogous Eu(III) and Tb(III) complexes, indicating equivalent residual hydration structures for Eu(III) and Tb(III) complexes of the same polyaminopolycarboxylate ligand.

Complexes of the simple polyaminotricarboxylates MEDTA, BEDTA, and HEDTA were found to possess approximately four waters of hydration. Lanthanide complexes of the polyaminotetracarboxylate ligands EDTA, PDTA, and CDTA contained approximately 2.5 inner sphere coordinated water molecules. While an increase in the steric constraints of the polyaminocarboxylate ligand (TMDTA or EDAP) did not result in a variation of the number of water molecules coordinated to the Eu(III) or Tb(III) ion, addition of ether functionalities (EGTA) or of an additional aminocarboxylate group (DTPA) reduced the Ln(III) hydration number to one. The non-integral number of coordinated water molecules suggests the presence of species with different extents of hydration in dynamic equilibrium. Since interchange between the different hydration states is “fast” on the luminescence time scale, the determined hydration numbers represent average values.

Lanthanide luminescence has also been used in the study of polyaza macrocyclic [38] and amide-based macrocyclic [39,40] chelates as possible MRI contrast agents. Kim et al. [38] used lanthanide luminescence lifetime measurements to determine the hydration numbers of Eu(III) or Tb(III) complexes with a series of tetraza macrocyclic ligands BP2A, PC2A, PCTA, and BPO4A (see Scheme 2 for ligand structure). The gadolinium analogues of these ligands were prepared and evaluated as possible MRI contrast enhancement agents. These workers excited the Eu(III) or Tb(III) excited state via absorption by pyridine moieties of the ligands and subsequent energy transfer into the excited state manifold of the chelated Ln(III) ion. For the Eu(III) and Tb(III) complexes of BPO4A, the Ln(III) ions were found to coordinate less than one water molecule on average. The Eu(III) and Tb(III) ions in the remaining complexes had between three and four water molecules in their primary coordination sphere.

In addition to luminescence lifetime techniques, the hydration of Ln(III)–polyaminopolycarboxylate complexes may also be investigated by nuclear



(a) $R_{1\text{-}3} = CH_2CO_2H$, $R_4 = CH_3$, n = 2
N-methylethylenediaminetriacetic acid (MEDTA)

(b) $R_{1\text{-}3} = CH_2CO_2H$, $R_4 = CH_2C_6H_5$, n = 2
N-benzylethylenediaminetriacetic acid (BEDTA)

(c) $R_{1\text{-}3} = CH_2CO_2H$, $R_4 = C_2H_4OH$, n = 2
N-hydroxyethylenediaminetriacetic acid (HEDTA)

(d) $R_{1\text{-}4} = CH_2CO_2H$, n = 2
ethylenediaminetetraacetic acid (EDTA)

(e) $R_{1\text{-}2} = CH_2CO_2H$; $R_{3\text{-}4} = C_2H_4CO_2H$, n = 2
ethylenediamine-*N*,*N'*-diacetic-*N*,*N'*-dipropionic acid (EDAP)

(f) $R_{1\text{-}4} = CH_2CO_2H$, n = 3
1,3-diaminopropanetetracetic acid (TMDTA)

a) $R_{1\text{-}4} = CH_2CO_2H$, $R_5 = CH_2CHCH_3$
1,2-diaminopropanetetraacetic acid (PDTA)

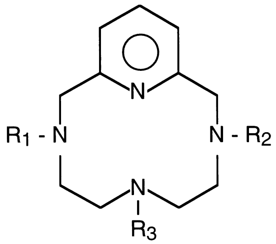
b) $R_{1\text{-}4} = CH_2CO_2H$, $R_5 = C_6H_{10}$
trans-1,2-diaminocyclohexanetetraacetic acid (CDTA)

a) $R_{1\text{-}4} = CH_2CO_2H$, n = 2
ethylenebisoxyethylenenitrilotetraacetic acid (EGTA)

a) $R_{1\text{-}5} = CH_2CO_2H$, n = 2
diethylenetriaminepentaacetic acid (DTPA)

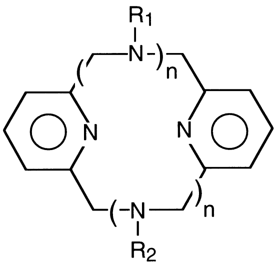
Scheme 1.

magnetic relaxation dispersion (NMRD) and relaxivity studies. The results of these types of studies have been shown to correlate well with hydration numbers determined from luminescence data for lanthanide complexes possessing at least one



a) $R_{1\text{-}2} = CH_2CO_2H$, R_3 = H
3,6,9,15-tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene -3,9-diacetic acid (PC2A)

b) $R_{1\text{-}3} = CH_2CO_2H$
3,6,9,15-tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene -3,6,9-triacetic acid (PCTA)



a) $R_{1\text{-}2} = CH_2CO_2H$, n = 1
2,11-diaza[3.3](2,6)pyridinophane-*N,N'*-diacetic acid (BP2A)

b) $R_{1\text{-}3} = CH_2CO_2H$, n = 2
2,5,14,17-tetraaza[3.3](2,6)pyridinophane -*N,N',N'',N'''*-tetraacetic acid (BPO4A)

Scheme 2.

inner sphere coordinated water molecule [38,41]. In particular, Brittain et al. [37] determined that the measured T_2 values (the longitudinal relaxation time) of several Gd(III)–polyaminopolycarboxylate complexes were linearly correlated with the hydration values of the corresponding Eu(III) complexes.

3.5. Lanthanide hydration numbers in polyelectrolytes

Naturally occurring organic acids such as fulvic acid or humic acid are polyelectrolytes and can function as important mediators of metal ion mobility in the environment. Due to the complex structure of these polyelectrolytes, their interaction with metal ions in the environment and the subsequent mobilization of the metal ions are not well understood [42]. The lanthanide ions, Eu(III) and Tb(III), may be used as luminescent probes of the structure of such complex molecules as well as of proteins [10,43] and other polyelectrolytes [44].

It is generally accepted that below pH 9 the carboxylate moiety is the most likely humate–material functional group to bind lanthanide cations [45]. Therefore, polymeric polycarboxylic acids, which possess well-defined structures, can serve as analogues for humic acid. The binding of Eu(III) ion in the polyacrylic acid {–[CH(COOH)CH$_2$]$_n$, PAA} as a function of pH and PAA molecular weight was studied by Lis et al. [46]. The authors used Eu(III) luminescence lifetimes to determine the hydration numbers of the PAA bound Eu(III) ions. As the pH of the solution was increased above 3, which coincides with the onset of the carboxylate group deprotonation, the hydration numbers dropped significantly. In the range pH 4–10, the residual hydration numbers were approximately 3 and were independent of the polyelectrolyte molecular weight. From these constant hydration numbers and the existence of a single peak in the $^5D_0 \rightarrow {}^7F_0$ excitation spectra over the same pH range, the authors concluded that each Eu(III) ion is complexed by three carboxylate moieties of the PAA molecule.

Luminescence lifetime measurements have also been used by Takahashi et al. [47] to determine the number of water molecules bound to Eu(III) ion in polymaleic acid {–[CH(C)H)]$_n$, PMA} and PAA complexes as a function of solution pH. Above pH 3, the hydration numbers for the PAA and PMA complexes ranged from 3.5 to 4.5 (in reasonable agreement with the work of Lis et al. [46]) with higher values of n generally observed for the PMA complexes. The differences in the hydration for the Eu(III)–PAA and –PMA complexes was attributed to the lower charge density of PAA relative to PMA. This would allow the PAA macromolecule to assume conformations in which more carboxylate groups were able to bind to the Eu(III) ion.

Dobbs et al. [48] used time-resolved lanthanide luminescence to study the binding of Eu(III) ion by fulvic acid. The intensities of the $^5D_0 \rightarrow {}^7F_1$ transition (592 nm) and the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (616 nm) of Eu(III) ion were used to determine the ratio of free to bound Eu(III). The intensity of the hypersensitive transition increased as the extent of Eu(III)–fulvic acid binding increased. The Eu(III) transition at 592 nm, which is not hypersensitive, exhibited essentially constant intensity with varying metal ion complexation. Using the intensity ratios of the Eu(III) emission, the authors were able to determine the concentration of uncomplexed Eu(III) over a range of experimental concentrations. These results were incorporated into a multiple-ligand model description of the binding of lanthanide ions by humic substances.

4. Eu(III) $^5D_0 \rightarrow {}^7F_0$ excitation spectroscopy

Empirical relationships have been developed between the frequency, υ, of the Eu(III) $^7F_0 \rightarrow {}^5D_0$ transition and the coordination around the metal ion. Several researchers [17,49,50] have reported a decrease in the frequency of the Eu(III)

$^7F_0 \rightarrow {}^5D_0$ band as the coordination ability of the ligand increased. Albin and Horrocks [51] first proposed a quantitative correlation between the total formal ligand charge and the frequency of the Eu(III) $^7F_0 \rightarrow {}^5D_0$ transition. They attributed the correlation to a decrease in the effective charge of the Eu(III) metal ion by the binding of the negatively charged ligand.

However, there were problems with the correlations of the calculated formal charge of the ligand in many systems and the observed shift in the Eu(III) $^7F_0 \rightarrow {}^5D_0$ frequency. The relationship proposed by Albin and Horrocks [51] provides good estimates of the $^7F_0 \rightarrow {}^5D_0$ frequency for systems with negatively charged donor groups, but does not seem to work for ligands in which the donor groups are neutral or in which a portion of the anionic groups is not bound to the metal center. The shift in the Eu(III) $^7F_0 \rightarrow {}^5D_0$ frequency has now been correlated with the number of bound donor groups by Choppin and Wang [52]. They determined the shift of the Eu(III) $^7F_0 \rightarrow {}^5D_0$ frequency for several mono-, di-, tri-, tetra-, and hexacarboxylic acids, aminocarboxylic acids, and oxocarboxylic acids relative to the free Eu(III)$_{aq}$ ion. The maximum ligand coordination number, CN_L, was found to be linearly related to the shift of the Eu(III) $^7F_0 \rightarrow {}^5D_0$ band, Δv, by Eq. (5). The use of Eq. (5) along with the determination of the Eu(III) ion hydration number by luminescence lifetime measurements permits the complete evaluation of the inner coordination sphere of the Eu(III) ion.

$$CN_L = 0.237\Delta v + 0.628 \tag{5}$$

The frequency of the $^7F_0 \rightarrow {}^5D_0$ transition in Eu(III) complexes has also been found by Frey and Horrocks [53] to correlate with the sum of the derived nephelauxetic parameters of the coordinating atoms.

Latva et al. [54] employed Eu(III) $^5D_0 \rightarrow {}^7F_0$ excitation spectroscopy to study the solution structure of chelates containing nitrogen heteroatoms of pyridine, pyrazole, and thiazole moieties. The authors determined the shifts in the $^5D_0 \rightarrow {}^7F_0$ excitation spectra for these different chelates and used the correlation developed by Frey and Horrocks [53] to calculate the shift parameters for the different types of nitrogen heteroatoms. The spectral shifts were attributed to variation in the distances between the nitrogen atoms and Eu(III) ion in the complexes of the different chelates.

Variations in the number and shape of the spectral features in the Eu(III) $^7F_0 \rightarrow {}^5D_0$ excitation spectrum have been used in the quantitative study of lanthanide complexation. Wu and Horrocks [49] have developed a method for the determination of stability constants of lanthanide complexes which utilizes excitation spectroscopy of the Eu(III) 0–0 transition to follow ligand–ligand competitive binding. Using EDTA as a reference ligand, these researchers determined the formation constants of 1:1 Eu(III) complexes with HEDTA, DTPA, and DO3A which agreed well with reported literature values.

The speciation of Eu(III) with the tridentate oxydiacetic acid (ODA) ligand was determined by Maupin et al. [55] using $^7F_0 \rightarrow {}^5D_0$ excitation spectroscopy. The authors determined the concentration of the mono-, bis-, and tris-ODA Eu(III) complexes by fitting the 0–0 excitation spectra to a Lorentzian lineshape at differing metal:ligand ratios. Representative Eu(III) $^7F_0 \rightarrow ^5D_0$ excitation spectra at different Eu(III):ODA ratios are presented in Fig. 2. At the lowest ligand ratio a single peak corresponding to Eu(ODA)$^{1+}$ complex was observed. As the ligand concentration was increased, additional features due to the Eu(ODA)$_2^{1-}$ and Eu(ODA)$_3^{3-}$ species appeared in the excitation spectrum.

Excitation spectra of the $^7F_0 \rightarrow ^5D_0$ Eu(III) band, as well as luminescence lifetime measurements, have been utilized to further the understanding of coordination of Eu(III) with ethylenediaminetetraacetic acid (EDTA). EDTA is a simple polyamino-polycarboxylate, but the structure of its Ln(III) complexes over a range of differing solution pH and concentrations is not well known. The 0–0 band of the excitation spectrum of aqueous solutions of Eu–EDTA has been found to exhibit two narrow components [22,56,57]. Based upon their observations at different temperatures, solution pH, and solution compositions, Dexpert-Ghys et al. [56] concluded that only two species were present in solution: Eu–EDTA$\cdot n$H$_2$O and Eu–(EDTA)$_2$. In a later study, Latva et al. deconvoluted the Eu(III) 0–0 bands using a Lorentzian–Gaussian peak shape [57]. These workers also found that EDTA forms 1:1 and 1:2 complexes with the Eu(III) ion, and also concluded that three 1:1 complexes, which differed in the number of coordinated water molecules, total coordination number, and complex geometry, were present in solution.

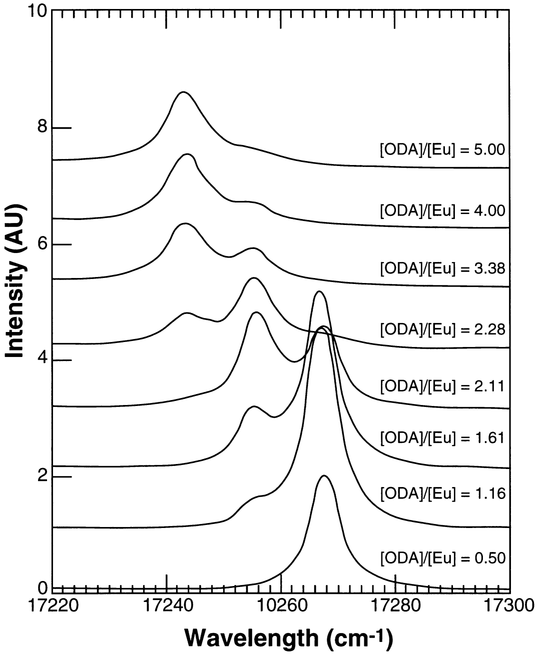


Fig. 2. $^7F_0 \rightarrow ^5D_0$ Eu(III) excitation spectra for solutions containing various [Eu(III)]:[oxydiacetate] ratios. [Eu(III)]$_T$ = 0.020 M. Adapted from ref. [55].

5. Ligand sensitized lanthanide luminescence

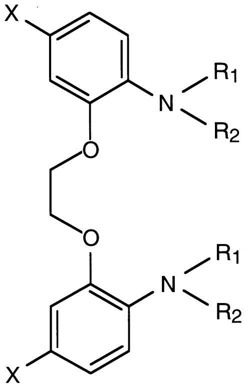
In general, the low intensities and quantum efficiencies of lanthanide luminescence in solution makes luminescence techniques difficult. To a large extent these disadvantages may be overcome by utilizing energy transfer to enhance the lanthanide luminescence. In this case intense luminescence originates from the transfer of energy from an excited state of an organic ligand to the emitting state of the Ln(III) ion. In order for efficient sensitized emission to occur, several requirements must be fulfilled. The chelate must effectively shield the Ln(III) ion from non-radiative decay processes such as coupling to the high energy vibrational modes of solvent molecules. The ligands should possess one or more chromophores with high molar extinction coefficients ($\epsilon > 10\,000$) and these chromophores must be able to effectively transfer energy into the Ln(III) ion excited states. In addition, the Ln(III) chelate should be thermodynamically stable, kinetically inert on the luminescent time scale, and soluble in aqueous systems.

Intramolecular energy transfer from a complexed ligand or intermolecular energy transfer due to collisions in solution may occur. This energy transfer generally takes place via the triplet levels in the chromophore and has been termed the "antenna" effect. The energy of the triplet level should be slightly higher than the Ln(III) emitting level. If the triplet energy is lower, back-transfer from the metal ion to the ligand occurs, reducing the efficiency of the sensitized emission. By the judicious choice of ligand, the luminescent properties of the metal ion may be optimized, which has been a major theme in the development of luminescent lanthanide compounds. Among the many reviews of the antenna effect in encapsulated lanthanide complexes, that of Sabbatini et al. [58] provides a discussion of a variety of macrocyclic systems which exhibit Eu^{3+} or Tb^{3+} sensitized luminescence.

For effective lanthanide sensitized emission to occur, the quenching effect of coordinated solvent molecules must be minimized. In the fluoroimmunoassay application, dissociation enhanced lanthanide fluoroimmunoassay (DELFIA) [11], this is accomplished by attaching the organic sensitizer to the lanthanide labeled immunocomplex after removal of the complex from the solvent. Therefore, the elimination of quenching of water molecules requires the isolation of the immunocomplex prior to complexation with the luminescence sensitizer. An alternative approach is to utilize ligands which saturate the coordination sites of the lanthanide metal in addition to a luminescence sensitizer which serves to transfer energy into the lanthanide ion luminescent state.

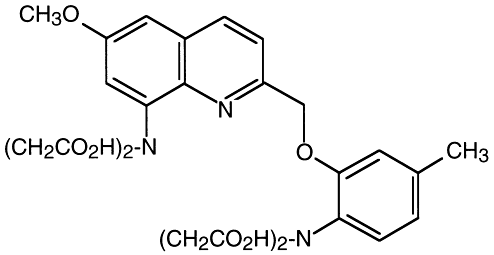
Coates et al. [59,60] have reported the enhancement of Eu(III) luminescence by the formation of mixed ligand complexes. These workers used derivatives of 1,10-phenanthroline-2,9-dicarboxylic acid or 2,2′:6′,2″-terpyridine-6,6″-dicarboxylic acid as sensitizers and several derivatives of EDTA to occupy the remaining coordination sites of the Eu(III) ion. The EDTA derivatives form Eu(III) complexes, which retain approximately three water molecules in the inner coordination sphere of the metal ion and do not exhibit ligand sensitized luminescence. The formation of the mixed ligand complex with a sensitizer ligand removes the remaining water molecules from the metal ion, resulting in rapid onset of metal centered luminescence.

Hoshino et al. [61] used aromatic polyaminocarboxylate ligands both to sensitize the lanthanide luminescence and to shield the lanthanide from the quenching effects of solvent molecules. The ligands contain aromatic chromophores which act as the "antenna" moieties for the sensitized lanthanide luminescence. The BAPTA and F-BAPTA ligands (see Scheme 3) form luminescent complexes with Tb(III) and Dy(III) ions while the QUIN 2 (see Scheme 3) ligand formed luminescent complexes with Sm(III) and Eu(III). Since BAPTA, F-BAPTA, and QUIN 2 are octadentate ligands, the majority of the water molecules are removed from the Ln(III) ion inner sphere. As a consequence, the quenching effects of coordinated water molecules are minimized. The Ln(III) luminescence intensity was enhanced by factors of 1600 and 1380 for the Tb(III)–BAPTA and Eu(III)–QUIN 2 complexes, respectively, relative to the intensity observed for the aquated metal ions.



a) $R_{1\text{-}2} = CH_2CO_2H$, X = H
1,2-bis(2-aminophenoxy)ethane-*N,N,N′,N′*-tetraacetic acid (BAPTA)

b) $R_{1\text{-}2} = CH_2CO_2H$, X = F
1,2-bis(2-amino-5-fluorophenoxy)ethane-*N,N,N′,N′*-tetraacetic acid (F-BAPTA)



a) 2[(2-amino-5-methylphenoxy)methyl]-6-methoxy-8-aminoquinoline -*N,N,N′,N′*-tetraacetic acid

Scheme 3.

6. Conclusions

In this review we have reviewed the utility of lanthanide luminescence spectroscopy in the study of lanthanide coordination chemistry. The availability of reliable laser systems capable of operating in the UV, visible, and infrared regions of the spectrum has allowed the techniques discussed in this review to become widely available. Luminescence lifetime measurements can provide valuable information about the hydration structure of Ln(III) metal ions in aqueous and non-aqueous solutions. Excitation spectroscopy of the $^7F_0 \rightarrow {}^5D_0$ Eu(III) band can provide details about the number of chemical environments of the Eu(III) ion and quantitative relationships have been developed which yield predictions of ligand coordination numbers. Through the use of these techniques, detailed knowledge of the coordination chemistry of lanthanide ions has been developed.

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