

Modification of the Luminescence Properties of an Europium(III) Tris(β -diketonate) Complex by Inclusion in γ -cyclodextrin and 2,3,6-trimethyl- γ -cyclodextrin

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Abstract

A 1:1 inclusion compound between octakis(2,3,6-tri-*O*-methyl)- γ -cyclodextrin (TRIMEG) and the chelate complex $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (NTA = 1-(2-naphthoyl)-3,3,3-trifluoroacetate) was prepared and characterized by powder X-ray diffraction, thermogravimetric analysis and photoluminescence spectroscopy. The results were compared with those obtained for the corresponding native γ -CD adduct. Excitation and emission spectra were measured, and the lifetimes were determined for the Eu^{3+} first excited state ($^5\text{D}_0$). The results indicate the presence of only one low-symmetry environment for the Eu^{3+} cations in the inclusion compounds. Encapsulation of the Europium complex in the two CDs increases the quantum efficiency of the ligand-to-metal energy transfer pathway, but the efficiency of the Eu^{3+} sensitization was significantly higher with TRIMEG as the host molecule. This may be related with the observation that the two hosts appear to have different influences on the Eu^{3+} coordination environments for the guest molecule.

Introduction

For some time there has been considerable interest in the luminescence and lasing ability of lanthanide complexes bearing β -diketone ligands [1]. A major goal is the synthesis of stable compounds that will function as efficient light conversion molecular devices [1c]. The complexes should have strong ligand-centered absorption in the UV region, efficient ligand to metal energy transfer rates, and intense metal-centered emission in the visible range, red for Eu^{III} and green for Tb^{III} [2]. Several highly luminescent tris(β -diketonate) complexes with the general formulae $\text{Ln}(\text{diket})_3\text{L}_n$ have been obtained by tuning the nature of the first-sphere ligands, e.g. the substituents on the β -diketone ligand or the Lewis base adducting molecule (L) [1d, 3]. A further approach to modify the photophysical properties of lanthanide complexes relies on 'soft' chemistry, that is, the immobilization of the complex in an inorganic, organic or hybrid inorganic–organic host. Examples of suitable hosts include zeolites [4], mesoporous materials [5], cyclodextrins (CDs) [6], liquid crystals [7] and di-ureasils [8].

In the case of CDs, the host can be considered as a second-sphere ligand non-covalently bonded to the first-sphere ligands [9]. Luminescence studies revealed that

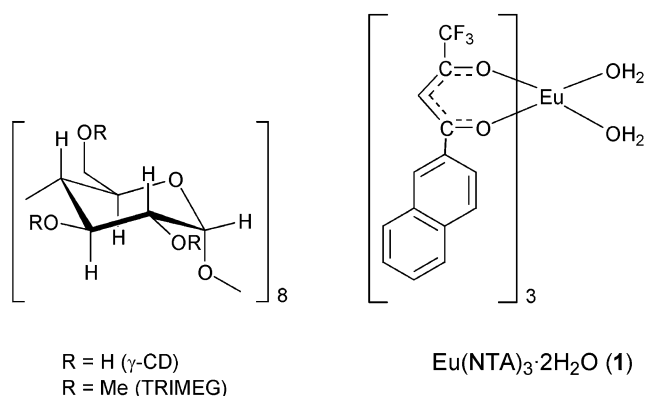
the encapsulation of the complex $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**) in β -CD induces emission from the singlet excited state of the ligands, with the corresponding inefficiency of the ligand-to-metal energy transfer step [6b]. It was proposed that steric effects, arising from the restricted space available for the guest NTA groups in the β -CD cavity, might be linked with these changes. A subsequent preliminary investigation seemed to support this idea, by showing that encapsulation of $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ in γ -CD, which has a cavity diameter of 7.9 Å compared with 6.2 Å for β -CD, actually induces a more efficient ligand-to-metal ion energy transfer pathway [6c]. We now wish to report that the efficiency of the Eu^{3+} sensitization can be further enhanced by using the alkylated cyclodextrin octakis(2,3,6-tri-*O*-methyl)- γ -CD (TRIMEG) as the host, rather than γ -CD (Scheme 1), and this paper describes a detailed comparison of the photophysical properties of the two inclusion compounds.

Experimental

Materials and methods

γ -CD hydrate (Wacker-Chemie) and TRIMEG (Cyclolab) were obtained from commercial sources and

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Scheme 1. Structural representation of the hosts and the guest (**1**) studied in this work.

used as received. The complex $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**) was prepared following a literature method [10]. Thermogravimetric analysis (TGA) studies were performed under air (30 mL min^{-1}) using a Shimadzu TGA-50 analyzer, with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The photoluminescence and lifetime measurements were recorded at room temperature on a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Jobin Yvon-Spex) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. All of the photoluminescence spectra were corrected for optics and detection spectral response. The solid samples were pressed into pellets and the measurements were carried out directly on the pellet surface.

Synthesis of $\gamma\text{-CD} \cdot \text{Eu}(\text{NTA})_3$ inclusion compound (**2**)

A solution of $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**) (200 mg, 0.203 mmol) in ethanol (3.0 ml) was added dropwise to a solution of $\gamma\text{-CD}$ (264 mg, 0.203 mmol) in water (2.0 ml), and the mixture stirred at room temperature for 1 h. The resulting pale yellow precipitate was filtered, washed with water and dried in air at room temperature (213 mg, 43%). Anal. Calcd. for $(\text{C}_{48}\text{H}_{80}\text{O}_{40}) \cdot (\text{C}_{42}\text{H}_{28}\text{F}_9\text{O}_8\text{Eu}) \cdot 10\text{H}_2\text{O}$ (2460.9): C, 43.89; H, 5.24; Eu, 6.21. Found: C, 43.66; H, 5.65; Eu, 7.46%.

Synthesis of TRIMEG $\cdot \text{Eu}(\text{NTA})_3$ inclusion compound (**3**)

A solution of $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**) (50 mg, 0.051 mmol) in ethanol (5.0 ml) was treated stepwise with solid TRIMEG (83.1 mg, 0.051 mmol). A little water (0.5 ml) was added to assist TRIMEG dissolution and the mixture was stirred at room temperature for 30 min. Evaporation of the solvents led to the isolation of a yellow powder. Anal. Calcd. for $(\text{C}_{72}\text{H}_{128}\text{O}_{40}) \cdot (\text{C}_{42}\text{H}_{28}\text{F}_9\text{O}_8\text{Eu}) \cdot 5\text{H}_2\text{O}$ (2707.5): C, 50.57; H, 6.18. Found: C, 50.00; H, 6.08%.

Results and discussion

The adduct comprising $\gamma\text{-CD}$ and $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**), designated as $\gamma\text{-CD} \cdot \text{Eu}(\text{NTA})_3$ (**2**), precipitates as a pale

yellow powder upon treatment of a saturated aqueous solution of $\gamma\text{-CD}$ with a solution of the complex in ethanol [6c]. Elemental analysis indicates that the host:guest molar ratio in the product is always close to 1:1, even when an excess of $\gamma\text{-CD}$ is used. This contradicts previous *ab initio* calculations which suggested that 3:1 (host:guest) inclusion compounds may be feasible in addition to the 1:1 stoichiometry, by inclusion of each of the three naphthalene fragments in a separate $\gamma\text{-CD}$ molecule [6c]. However, these calculations were performed considering a 3:1 adduct in vacuum, and the failure to isolate a crystalline 3:1 adduct in the solid-state may be due to the impossibility of a stable crystal packing arrangement. The 1:1 TRIMEG inclusion compound, TRIMEG $\cdot \text{Eu}(\text{NTA})_3$ (**3**), is much more soluble than the corresponding $\gamma\text{-CD}$ adduct and was therefore isolated by evaporation of the reaction solution to dryness.

Powder X-ray diffraction shows that compound **3** is mainly amorphous (not shown), while compound **2** is microcrystalline [6c]. Neither pattern contains peaks assignable to native $\gamma\text{-CD}$ hydrate nor bulk $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**), which is an initial indication for the formation of true inclusion compounds [11]. A microcrystalline $\gamma\text{-CD}$ adduct containing the gadolinium complex $\text{Gd}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ was also prepared, but the powder XRD pattern was considerably different from that for **2**. This implies that the crystal packing arrangements in the two inclusion compounds are different, and we may therefore assume that the first and second-sphere coordination geometries for the lanthanide ions are also different for the two inclusion compounds. As a result, the Gd compound cannot be used as a model to study the electronic states in compound **2**.

Figure 1a shows the TGA curves for $\gamma\text{-CD} \cdot \text{Eu}(\text{NTA})_3$ (**2**), $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (**1**), pristine $\gamma\text{-CD}$ hydrate and a physical mixture of $\gamma\text{-CD}$ and **1** in a 1:1 molar ratio. $\gamma\text{-CD}$ dehydrates up to $110 \text{ }^\circ\text{C}$ (10%, 7–8 water molecules per $\gamma\text{-CD}$ molecule), starts to melt and decompose at $260 \text{ }^\circ\text{C}$, and at $500 \text{ }^\circ\text{C}$ 100% mass loss is reached. Compound **1** undergoes partial dehydration up to $75 \text{ }^\circ\text{C}$ (1.7%, which corresponds to about 1 water molecule per complex molecule), and then decomposes in two steps up to $500 \text{ }^\circ\text{C}$, leaving a residual mass of 16.9%. Decomposition of the inclusion compound **2** takes place in two main steps up to $450 \text{ }^\circ\text{C}$, and the onset of decomposition ($190 \text{ }^\circ\text{C}$) is intermediate between that of **1** ($120 \text{ }^\circ\text{C}$) and $\gamma\text{-CD}$. Overall, the TG behavior of **2** is quite similar to that found previously for the corresponding $\beta\text{-CD}$ adduct [6b]. Surprisingly, the TGA curve for the physical mixture is not very different from that for **2**. If the two components behaved independently, decomposition of the 'free' lanthanide complex should be noticeable above $150 \text{ }^\circ\text{C}$. However, no clear inflection is observed up to $200 \text{ }^\circ\text{C}$ and the trace is almost superimposable with that for the inclusion compound. This is in sharp contrast to the behavior exhibited by the corresponding physical mixture of $\beta\text{-CD}$ and **1**, where each component behaves independently [6b]. Grinding $\gamma\text{-CD}$

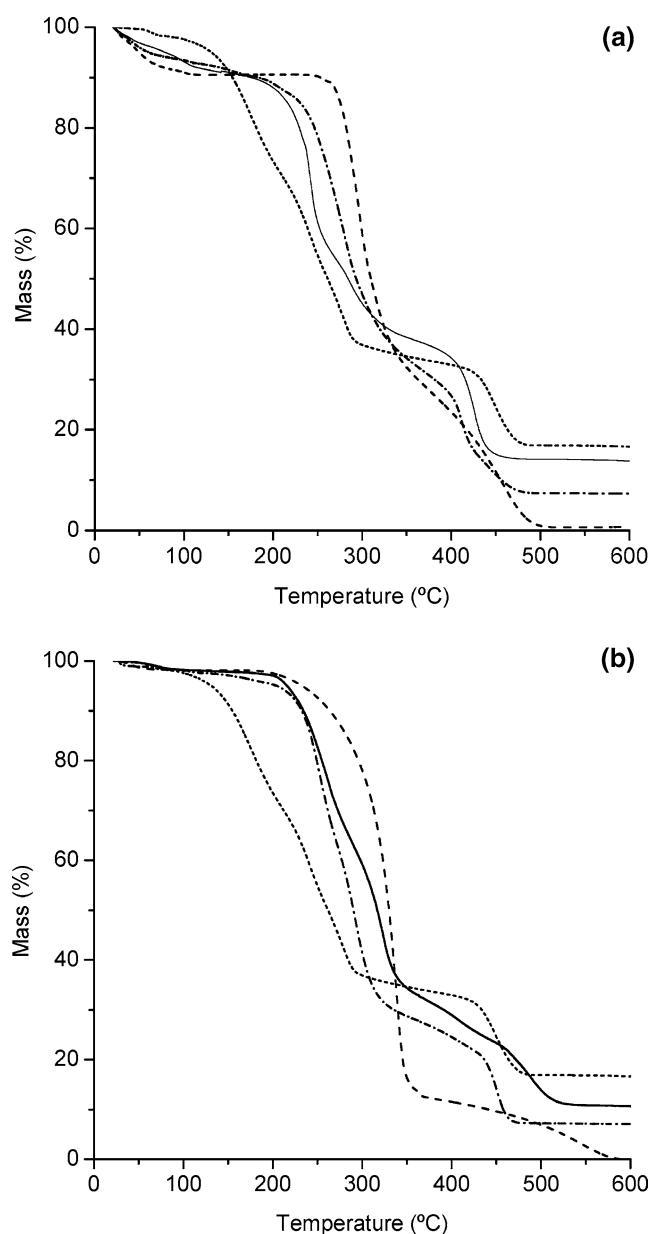


Figure 1. TGA of (a) the inclusion compound γ -CD·Eu(NTA)₃ (**2**) (—), Eu(NTA)₃·2H₂O (**1**) (·····), pristine γ -CD hydrate (---) and a 1:1 physical mixture of γ -CD and **1** (-·-·-), and (b) the inclusion compound TRIMEG·Eu(NTA)₃ (**3**) (—), compound **1** (·····), TRIMEG (---) and a 1:1 physical mixture of TRIMEG and **1** (-·-·-).

and **1** together followed by mild heating (up to 100 °C) may be sufficient to induce an interaction between the two components, with the result that the thermal behavior towards higher temperatures is comparable with that for the inclusion compound **2**. This kind of behavior was also evident for the system containing complex **1** and TRIMEG (Figure 1b). The main difference between the TGA curves for **2** and **3** is in the dehydration behavior. Thus, at 120 °C, the mass loss is 8.2% for **2** (ca. 11 molecules per formula unit), and 2.0% for **3** (ca. 3 water molecules per formula unit).

Figure 2 shows the excitation spectra for compounds γ -CD·Eu(NTA)₃ (**2**) and TRIMEG·Eu(NTA)₃ (**3**)

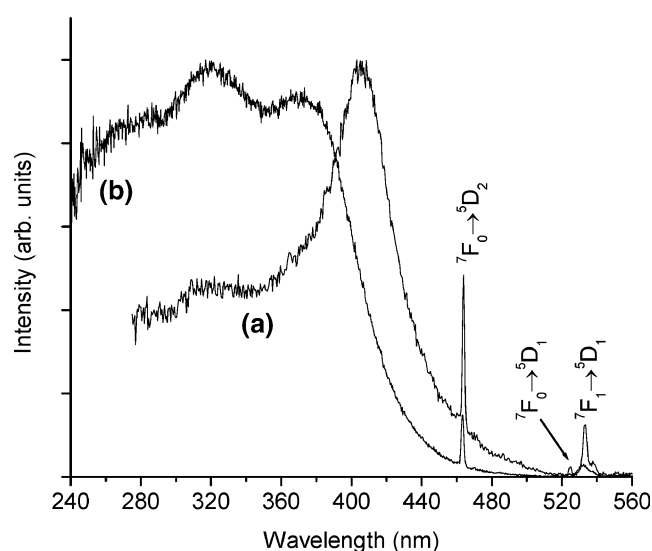


Figure 2. Excitation spectra for the compounds (a) γ -CD·Eu(NTA)₃ (**2**) and (b) TRIMEG·Eu(NTA)₃ (**3**) monitored around 611 nm.

monitored within the more intense line of the ${}^5D_0 \rightarrow {}^7F_2$ transition. The spectra contain a large broad band with three main components, overlapping two low-intensity Eu³⁺ intra-4f⁶ lines ascribed to transitions between the ${}^7F_{0,1}$ levels and upper states. For the γ -CD adduct, the peaks of the large broad band are centered around 280, 321 and 403 nm. The two higher energy components for the TRIMEG adduct are found at the same positions as those for the γ -CD adduct, but the lower energy component is blue-shifted to approximately 370 nm. A comparison of these spectra with the excitation spectrum of the starting complex, Eu(NTA)₃·2H₂O (**1**) [12], reveals a displacement in the lower energy region of the maximum of the broad band, which is more evident for the γ -CD adduct. This effect had already been observed for inclusion compounds involving β -CD and the same guest species [6b]. Another significant change in the excitation spectra monitored within the Eu³⁺ lines of the inclusion compounds with respect to those of complex **1** and the β -CD compounds is the appearance of at least two components peaking around 272 and 320 nm. The low intensity of the intra-4f⁶ lines with respect to that of the large broad band suggests that the Eu³⁺ excited levels are more efficiently populated *via* a sensitized process compared with direct excitation into the Eu³⁺ levels. For compound **2**, the ratio of the integrated intensities for the large broad band and the intra-4f⁶ lines is five times smaller than that for compound **3**, indicating that the TRIMEG host is much more effective in inducing efficient Eu³⁺ sensitization.

Figure 3 shows the emission spectra of γ -CD·Eu(NTA)₃ (**2**) and TRIMEG·Eu(NTA)₃ (**3**) obtained under the excitation wavelength that maximizes the emission intensity. The spectra display the typical Eu³⁺ intra-4f⁶ lines ascribed to transitions between the 5D_0 excited state and the ground multiplet, ${}^7F_{0-4}$. For both compounds, 1, 3 and 4 emission lines are observed for the ${}^5D_0 \rightarrow {}^7F_{0-2}$ transitions, respectively, suggesting a low site-symmetry

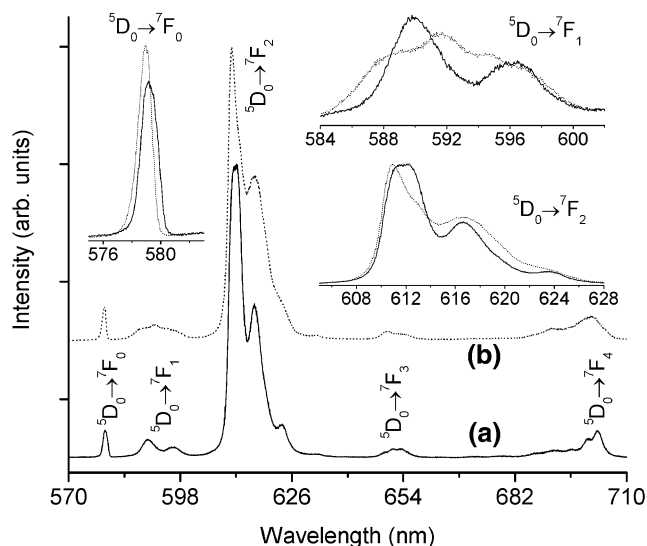


Figure 3. Emission spectra for the compounds (a) γ -CD·Eu(NTA)₃ (2) and (b) TRIMEG·Eu(NTA)₃ (3) excited around 403 and 321 nm, respectively.

group without an inversion center, in accordance with the higher intensity of the $^5D_0 \rightarrow ^7F_2$ transition. Since the $^5D_0 \rightarrow ^7F_0$ transition occurs between non-degenerate states, the presence of only one line indicates that all of the Eu^{3+} ions occupy the same local coordination environment within each sample. Moreover, changing the excitation wavelength to 321 nm does not significantly alter the energy and full-width-at-half-maximum (fwhm) of the intra- $4f^6$ lines. The energy of these lines is, however, different for the two inclusion compounds, which points to slightly different Eu^{3+} local coordination environments. Comparing the emission features of the inclusion compounds with those of the complex $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (1) [12], there is a red-shift of the $^5D_0 \rightarrow ^7F_0$ transition upon inclusion complexation, and changes are observed in the energy and fwhm of the Stark components. These changes imply that the Eu^{3+} local coordination geometry of the tris(β -ketonate)europium(III) complex undergoes slight alterations upon inclusion in the different CD hosts.

The lifetime of the Eu^{3+} first excited state (5D_0) was monitored around the $^5D_0 \rightarrow ^7F_2$ emission lines. As Figure 4 shows, the measured decay curves are well reproduced by a single exponential function revealing lifetime values of 0.442 ± 0.002 ms for γ -CD·Eu(NTA)₃ (2) and 0.322 ± 0.005 ms for TRIMEG·Eu(NTA)₃ (3). The lifetime measured for complex 1 is of the same order of magnitude, being around 0.35 ms [12]. The decay curves obtained for a lower excitation wavelength of 321 nm are identical to those depicted in Figure 4, confirming that all of the Eu^{3+} metal ions occupy the same average local environment within each sample. The different lifetime values obtained for the two compounds are consistent with the presence of different Eu^{3+} coordination spheres, in agreement with the photoluminescence spectra described above. In summary, γ -CD encapsulation of $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ (1) increases the

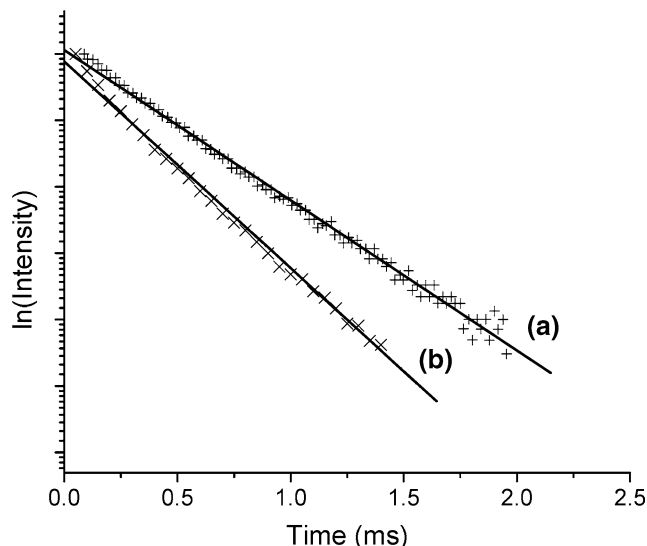


Figure 4. Emission decay curves for the compounds (a) γ -CD·Eu(NTA)₃ (2) and (b) TRIMEG·Eu(NTA)₃ (3) monitored around 611 nm, and excited around 403 and 321 nm, respectively. The solid lines are the best linear fits to the data ($R > 0.99$).

quantum efficiency of the ligand-to-metal energy transfer pathway (in contrast to that observed for β -CD). Furthermore, we have shown that the efficiency of the Eu^{3+} sensitization can be further increased by using permethylated γ -CD as the host rather than native γ -CD. Molecular modeling studies have shown that complete methylation of the hydroxyl groups on cyclodextrins can lead to an increase of both cavity opening and of internal diameter (glycosidic oxygens) [13]. The greatest increase was found for γ -cyclodextrin. Obviously, these changes are likely to be important with respect to the inclusion of the europium chelate molecule and the modification of its photophysical properties. Further work is underway in our laboratories in order to build on these results and explore the potential of TRIMEG as a second-sphere ligand for luminescent molecules.

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