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Study of the Inclusion Compound Formed between a Luminescent Europium(III) β-Diketonate Complex and γ-Cyclodextrin

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Abstract

A 1 : 1 inclusion compound between γ-CD and the tris chelate complex $Eu(NTA)_3 \cdot 2H_2O$ [NTA = 1-(2-naphthoyl)-3,3,3-trifluoroacetone)] was prepared and characterized in the solid-state by powder X-ray diffraction, thermogravimetric analysis, FTIR, ^{13}C CP MAS NMR and photoluminescence spectroscopy. Possible host-guest interaction geometries were generated from *ab initio* calculations. The photoluminescence results reveal the presence of a metal-to-ligand energy transfer that is much more efficient than that previously reported for the analogous β-CD adduct.

Introduction

The interaction of cyclodextrins (CDs) with metal complexes is an important phenomenon because, in the resulting inclusion compounds, the cyclodextrin host can be considered as a second-sphere ligand non-covalently bonded to the first sphere ligand(s) [1]. This offers the possibility of subtly modifying the properties of the guest, for example in their ligand substitution/insertion reactions [2] and photoluminescent properties [3]. The last example refers to the encapsulation of tris(dibenzoylmethane)europium(III) dihydrate by β-CD. We subsequently prepared inclusion compounds between β-CD and europium(III)/gadolinium(III) tris chelates of 1-(2-naphthoyl)-3,3,3-trifluoroacetone (NTA) [4]. This work followed on from a study of the luminescence features and the absolute quantum yields of europium(III) tris[1-(2-naphthoyl)-3,3,3-trifluoroacetonate] complexes, $Eu(NTA)_3 \cdot 2L$ (L = H_2O and DMSO, dimethyl sulfoxide) [5]. It was found that the DMSO adduct $Eu(NTA)_3 \cdot 2DMSO$ exhibits an experimental quantum yield of 0.75, one of the highest so far reported for solid-state europium complexes. In the present work we describe the preparation and characterization of an inclusion compound between γ-CD and $Eu(NTA)_3 \cdot 2H_2O$. In particular, the luminescence characteristics are compared with the corresponding β-CD complex. *Ab initio* calculations have also been performed to shed light on possible host-guest inclusion geometries.

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Experimental

Instrumentation and analysis

Infrared spectra were recorded with a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) studies were performed under air (30 mL min^{-1}) using a Shimadzu TGA-50 analyzer, with a heating rate of 1 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer using Cu-K_a radiation filtered by Ni ($\lambda = 1.5418$ Å). Microanalyses were performed at the Technical University of Munich. Room-temperature solid-state ^{13}C NMR spectra were recorded at 100.62 MHz on a (9.4 T) Bruker MSL 400P spectrometer. ^{13}C CP MAS NMR spectra were recorded with a 4.5 μs ^1H 90° pulse, 2 ms contact time, a spinning rate of 9 kHz and 12 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane (TMS). The photoluminescence spectra (14–300 K) were recorded on a Jobin Yvon-Spex spectrometer (HR 460) coupled to a R928 Hamamatsu photomultiplier. A 150 W Xe arc lamp coupled and a monochromator Jobin Yvon-Spex (TRIAX 180) was used as excitation source. All the spectra were corrected for the response of the detector. The time-resolved measurements were carried out using a pulsed Xe arc lamp (5 mJ/pulse, 3 ms bandwidth) coupled to the monochromator Kratos GM-252 and a Spex 1934 C phosphorimeter.

Synthesis

γ-CD was kindly supplied by Wacker-Chemie (Berlin, Germany) and used as received. 1-(2-Naphthoyl)-3,3,3-trifluoroacetone was purchased from Aldrich and used as

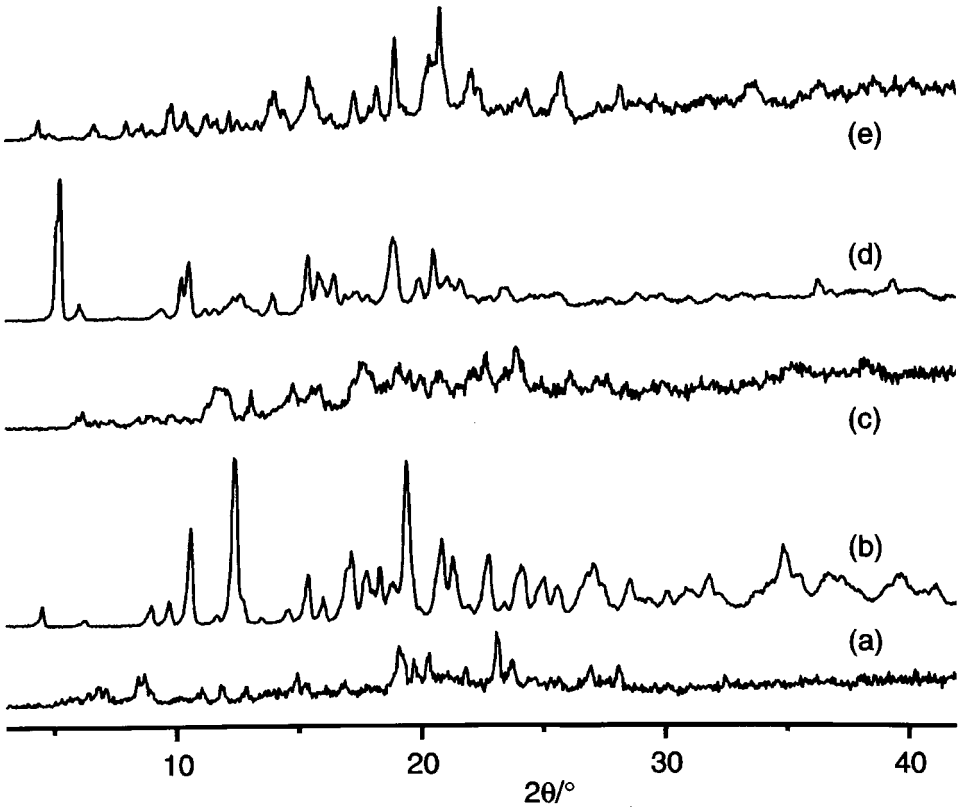

Figure 1. Powder XRD of (a) $Eu(NTA)_3{\cdot}2H_2O$ (**1**), (b) β-CD hydrate, (c) $Eu(NTA)_3 \cdot \beta$-CD (**2**), (d) γ-CD hydrate and (e) $Eu(NTA)_3 \cdot \gamma$-CD (**3**).

received. $Eu(NTA)_3{\cdot}2H_2O$ (**1**) was prepared as described in the literature [6]. IR, ^1H NMR and ^{13}C NMR data for **1** were in agreement with that reported previously [4]. The preparation and characterization of the 1 : 1 complex between β-CD and **1**, hereafter referred to as $Eu(NTA)_3 \cdot \beta$-CD (**2**), is described in detail in ref. [4]. The same method was used to prepare the corresponding compound with γ-CD, $Eu(NTA)_3 \cdot \gamma$-CD (**3**). Thus, a solution of $Eu(NTA)_3{\cdot}2H_2O$ (0.076 mmol) in ethanol (7 mL) was added dropwise to an aqueous solution (5 mL) of γ-CD (0.076 mmol) and the mixture kept at 40 °C for 30 min. The resulting suspension was centrifuged, the supernatant decanted, and the yellow microcrystalline powder washed with water and dried in a desiccator for several days (0.16 g, 91% yield). Anal. Calcd. for $(EuC_{42}H_{24}F_9O_6){\cdot}(C_{48}H_{80}O_{40}){\cdot}8H_2O$ (2388.9): C, 45.25; H, 5.06; Eu, 6.36. Found: C, 45.68; H, 5.15; Eu, 6.37. IR (KBr, cm^{-1}): 3057 (m), 2929 (m), 1638 (sh), 1620 (sh), 1611 (vs), 1593 (s), 1570 (s), 1534 (s), 1516 (s), 1511 (s), 1460 (s), 1431 (m), 1385 (m), 1355 (m), 1300 (vs), 1200 (s), 1187 (s), 1134 (vs), 1127 (vs), 1078 (m), 1026 (s), 959 (m), 937 (m), 868 (m), 796 (s), 766 (m), 745 (m), 685 (s), 571 (m), 520 (m), 472 (m), 354 (w). ^{13}C CP MAS NMR: δ = 133.5 (sh), 125.4 (br) (all naphth-C), 101.8 (γ-CD, C-1), 80.4 (γ-CD, C-4), 70.7 (γ-CD, C-2,3,5), 60.7 (γ-CD, C-6).

Results and discussion

Synthesis and characterization of γ-CD inclusion compound

Elemental analysis indicated a 1 : 1 host-to-guest stoichiometry for $Eu(NTA)_3 \cdot \gamma$-CD (**3**), as found previously for the corresponding β-CD adduct $Eu(NTA)_3 \cdot \beta$-CD (**2**). Compound **3** was further characterized in the solid-state by IR, powder XRD, TGA and ^{13}C CP MAS NMR. The two products **2** and **3** give rise to substantially different powder XRD patterns, and it is evident that neither compound contains measurable amounts of phases corresponding to either pure $Eu(NTA)_3{\cdot}2H_2O$ (**1**) or the corresponding pristine cyclodextrin hydrate (Figure 1). This is an initial indication for the formation of true inclusion compounds [7]. The γ-CD adduct **3** is more crystalline than **2** and in this respect is comparable to pristine γ-CD hydrate. TGA was also useful for the recognition of complex formation in **3** (not shown). Decomposition takes place in two steps up to 450 °C, the first of these occurring between 190 and 330 °C (51% mass loss), and the second between 400 and 450 °C (21% mass loss). The onset of decomposition (190 °C) is intermediate between that of **1** (120 °C) and γ-CD hydrate (which begins to melt and decompose at 260 °C). Loss of hydrated water occurs in the temperature range 25–150 °C (5.7%, ca. 8 water molecules per formula unit). Overall, the TG behavior of **3** is quite similar to that found previously for **2** [4]. The KBr IR spectrum of **3** shows the typical bands previously reported for bulk KBr spectra of β-CD, indicating no chemical modification of the cyclodextrin host [8]. In addition,

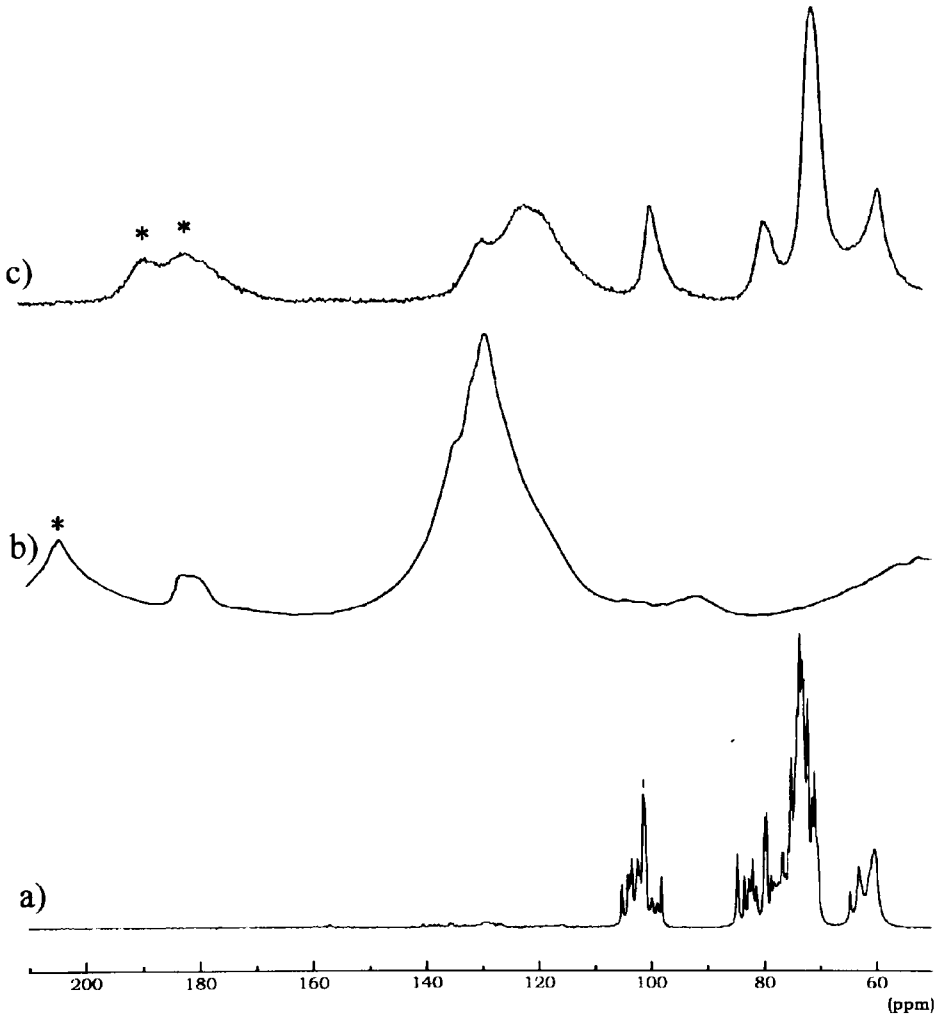

Figure 2. ^{13}C CP MAS NMR spectra of (a) γ-CD hydrate, (b) Eu(NTA)$_3$·2H$_2$O (**1**) and (c) Eu(NTA)$_3$ · γ-CD (**3**).

several characteristic absorption bands of the guest are observed. The small or nonexistent shifts in the positions of these bands relative to those of the "free" tris(β-diketonate) complex indicates that the structural integrity of **1** is largely retained upon inclusion complexation with γ-CD. It follows that the host : guest interactions are not particularly strong.

Figure 2 shows the ^{13}C CP MAS NMR spectrum of **3**, pristine γ-CD and the guest precursor Eu(NTA)$_3$·2H$_2$O (**1**). Like β-CD hydrate, γ-CD hydrate exhibits multiple resonances for each type of carbon atom, assigned to C-1 (98–105 ppm), C-4 (78–84 ppm), C-2,3,5 (71–76 ppm) and C-6 (60–64 ppm). This has been mainly correlated with different torsion angles about the (1 $\rightarrow$ 4) linkages for C-1 and C-4 [9a, b], and with torsion angles describing the orientation of the hydroxyl groups [9c]. By contrast, the corresponding carbons for **3** (and **2**) are observed as single broad peaks. A possible interpretation is that the conformation of the CD is more symmetrical in the complexes, with each glucose unit in a similar environment, as a consequence of the inclusion of aromatic groups in the host cavities [10, 11]. The spectrum of **3** also shows a broad peak centered at 125 ppm (with a shoulder at 134 ppm) due to the carbon atoms of the naphthalene groups. A peak for the methylene carbon atom of the chelate ring is not observed in the spectrum of **3** (expected at about 93 ppm).

Luminescence behavior

The 14 K emission spectra of both Eu(NTA)$_3$ · β-CD (**2**) and Eu(NTA)$_3$ · γ-CD (**3**), for the excitation wavelength that maximizes the cation luminescence intensity, are plotted in Figure 3. The spectra are composed of a series of yellow-red sharp lines, assigned to intra-4f^6 transitions between the ^{5}D$_0$ and the ^{7}F$_{0-4}$ levels, that overlap a large broad band in the purple-blue region (420–570 nm). This large broad band, associated with excited states of the ligands [4], is much more evident for **2**, suggesting that the inclusion of the complex into the γ-CD cavity induces a more efficient ligand-to-metal ion energy transfer pathway. This is confirmed by lifetime measurements. While for Eu(NTA)$_3$ · γ-CD the ^{5}D$_0$ decay curve is well fitted by a single-exponential function, corresponding to a lifetime around 0.40 ms, the decay profile of the Eu(NTA)$_3$ · β-CD compound unequivocally exhibits a non-exponential behavior for shorter times, associated with an energy transfer pathway involving the Eu^{3+} first coordination shell and the excited states of the ligands [4]. This inefficient energy transfer step present in the β-CD adduct

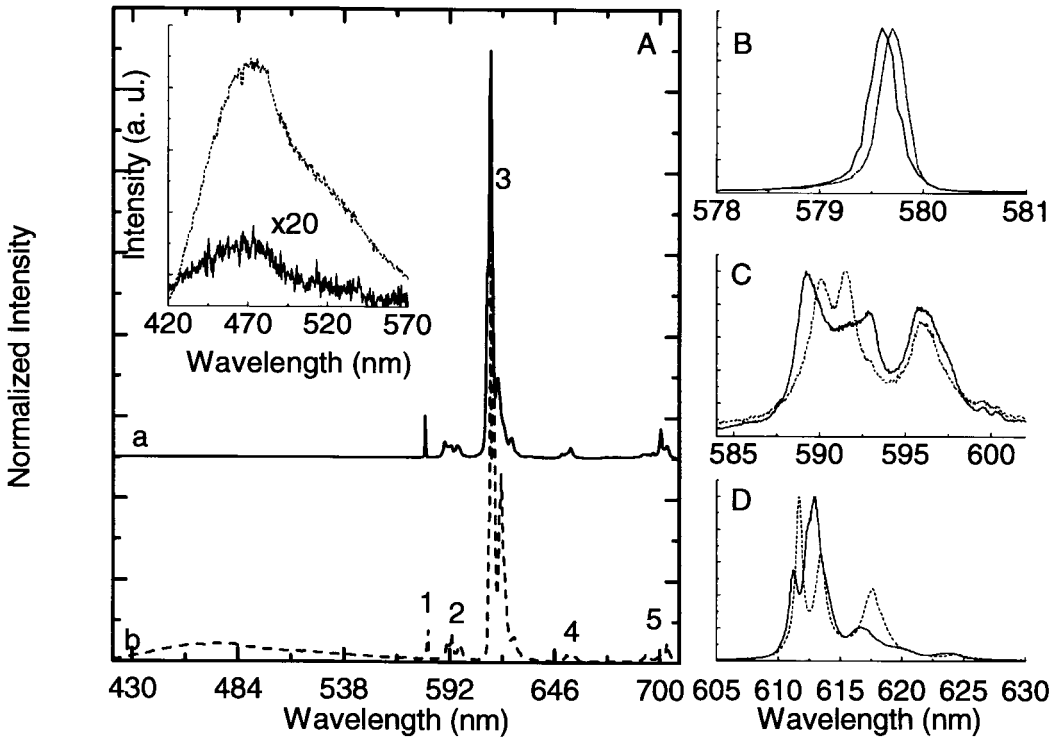

Figure 3. (A) Emission spectra (14 K) of Eu(NTA)$_3 \cdot \beta$-CD (**2**) (dashed line) and Eu(NTA)$_3 \cdot \gamma$-CD (**3**) (solid line), excited at 395 nm. (1), (2), (3), (4) and (5) denote the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions. The inset compares the relative intensity of the large broad band in both compounds. Figures B, C and D show, for the two inclusion compounds, the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions, respectively.

is not observed in the γ-CD complex, and as a result the latter exhibits an increase in the quantum efficiency.

Ab initio calculations

Ab initio calculations were carried out using the Gaussian98 program package, running on a personal computer. The modeling of both the free complex and the inclusion compound was performed by single point calculations scanning, using the point charge approach of Cundari *et al.* for the metallic center [12] and the two layer approximation of Morokuma *et al.* [13] (ONIOM keyword of Gaussian98) for the first and second ligand sphere (B3LYP : CEP-4G). Figure 4 shows the best geometry found for Eu(NTA)$_3 \cdot \gamma$-CD (**3**). The NTA ligands assume a propeller-like orientation, with the two water molecules above and below this framework. The calculations show that it is possible for each of the three naphthalene fragments to be included in a separate γ-CD molecule, suggesting that 1 : 3 inclusion compounds may be feasible in addition to the 1 : 1 compound reported here. This would not be surprising since 1 : 1 and 1 : 3 adducts were characterized previously with β-CD as the host [4].

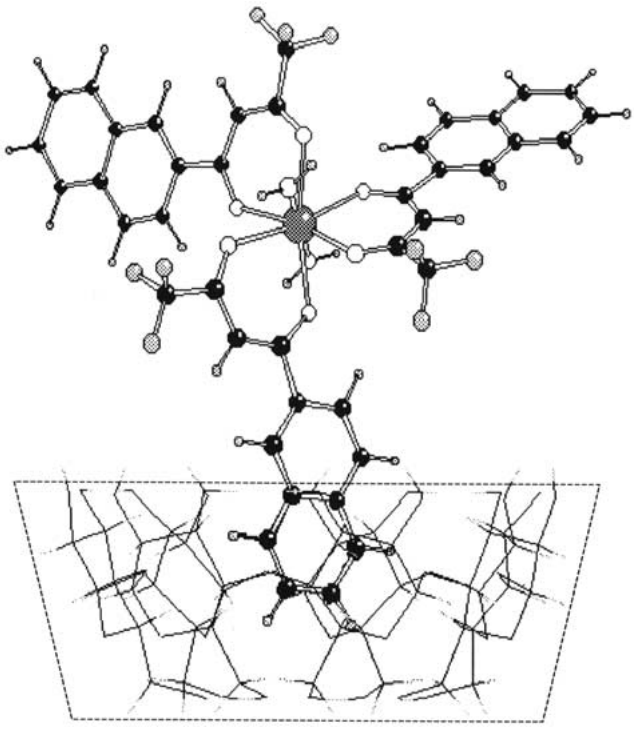

Figure 4. Ab initio structure of the lowest energy inclusion geometry for Eu(NTA)$_3 \cdot \gamma$-CD (**3**).

Conclusions

Eu(NTA)$_3 \cdot 2H_2O$ readily forms 1 : 1 inclusion compounds in the solid-state with both β- and γ-CD, as evidenced by elemental analysis, powder XRD, IR and ^{13}C CP MAS NMR spectroscopy, and supported by *ab initio* calculations. Although the host-guest interaction is weak, it has been shown that the photoluminescence properties of the guest are affected by the type of host (and also the host-guest stoichiometry). Further work will expand on this idea of using

inclusion chemistry to modify the luminescence properties of lanthanide complexes.

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