Dendritic lanthanide complexes and the effect of Lewis-acid encapsulation

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The synthesis of complexes using terbium(III) ions and dendritic branches based on L-lysine building blocks is reported. These complexes are bound *via* predominantly electrostatic lanthanide–carboxylate interactions, and were characterised using a range of approaches. The ability of these Lewis-acidic complexes and terbium acetate to influence the regiochemical outcome of a Diels–Alder reaction was investigated, but they were found to have minimal effect. Interestingly, however, non-dendritic terbium(III) acetate was observed to remain bound to the product of the reaction, broadening its NMR spectrum, whilst the dendritic terbium complexes did not interact in this way. This indicates that the Lewis-acidic centre in the more highly functionalised dendritic derivatives may be inaccessible, either sterically or electronically, both to substrates and products of organic transformations.

Introduction

Since their discovery, the lanthanides have been the focus of increasing interest. Their paramagnetism has made them ideal for widespread use in magnetic resonance imaging applications,[1] their optical properties make them of interest as optical contrast agents,[2] and their Lewis acidity has provided them with particular value to synthetic chemists.[3] Chiral ligands for lanthanides have been of interest as a way of endowing reactions with stereoselectivity, and a wide range of examples using this approach have been reported. Recently, lanthanide complexes using fluorinated ligands have been reported.[4] This type of ligand effectively encapsulates the lanthanide within a fluorous shell and allows it to be applied in the fluorous phase. This approach has assisted recycling of the Lewis-acid catalyst.

For some time, we have been interested in the effect of encapsulation on the behaviour of active sites. In particular, we and others, have argued that by encapsulating an active unit, it exhibits modified properties, with the surrounding organic shell mimicking the behaviour of a protein superstructure.[5] This approach has been applied to the modification of optical[6] and redox[7] properties using molecules which possess dendritic branching. Dendritically encapsulated catalysts for a variety of organic reactions have also been reported.[8] We therefore decided to synthesise some dendritically encapsulated lanthanide ions and investigate the effect of encapsulation on the Lewis-acid properties. Lanthanide-cored dendrimers have been reported previously by Kawa and Fréchet and co-workers[9] They used carboxylate–lanthanide interactions to assemble branches based on aromatic-ether repeat units around Er(III), Eu(III) and Tb(III) cores. They reported that the encapsulated core exhibited enhanced luminescence properties as the dendrimer size increased – an effect which was attributed both to the antenna effect and site isolation of the lanthanide. Lindgren and co-workers have also used carboxylate–lanthanide interactions to assemble dendritic structures, with a specific interest in photonic applications.[10] Zhu and co-workers investigated the coordination of Tb(III) to a linear-dendritic block co-polymer and again reported enhanced luminescence as the dendrimer size increased.[11] Meanwhile Vögtle, Balzani and co-workers have bound lanthanide ions within spherical dendrimers based on L-lysine as a consequence of interactions between the amide C=O groups and the lanthanide ion.[12] These spherical dendrimers did not possess a charged binding site for the lanthanide such as a carboxylate. However, in spite of the interest in optical properties described above, there are no previous reports of the effect of dendritic encapsulation on the Lewis acid properties of a lanthanide ion, and this was therefore a target of our research. We decided to monitor the effect of encapsulation by synthesising a dendritic complex using carboxylate–lanthanide electrostatic interactions (Fig. 1). We anticipated that the dendritic superstructure would play a role in controlling the activity of the encapsulated metal ion and hoped this might guide us towards new principles for catalyst design.
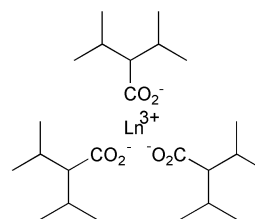

Fig. 1 Dendritic branches with carboxylate groups at the focal point bind lanthanides as a consequence of electrostatic interactions.

Results and discussion

Synthesis of complexes G1–Tb and G2–Tb

The methodology chosen for the synthesis of these dendrimer–lanthanide conjugates was analogous to that previously reported by Kawa and Fréchet.[9a] However, instead of using the carboxylic acid functionalised aromatic-ether type branches as reported by these authors, we decided to use dendritic branches based on L-lysine repeat units. These branches possess considerably more flexibility than those used by Kawa and Fréchet and co-workers,[9] which means they are more able to fold and have an impact on the core lanthanide cation. Furthermore, these amino-acid derived branches possess chiral centres – a feature which has potential use in synthetic methodology.

Dendritic branches **G1(COOH)** and **G2(COOH)** were synthesised using standard methodology, with characterisation being in agreement with data in the literature.[13] These dendritic branches were then assembled around the lanthanide core as outlined in Scheme 1.

Dehydrated terbium(III) acetate was refluxed with the carboxylic acid form of the dendrons in chlorobenzene. During this reaction, acetic acid was liberated and was continuously removed from the mixture using a Dean–Stark apparatus (155 °C) in order to encourage complexation of the carboxylate ligands. At the end of the reaction, the mixture was evaporated to dryness to yield a yellow glassy solid. It was important that
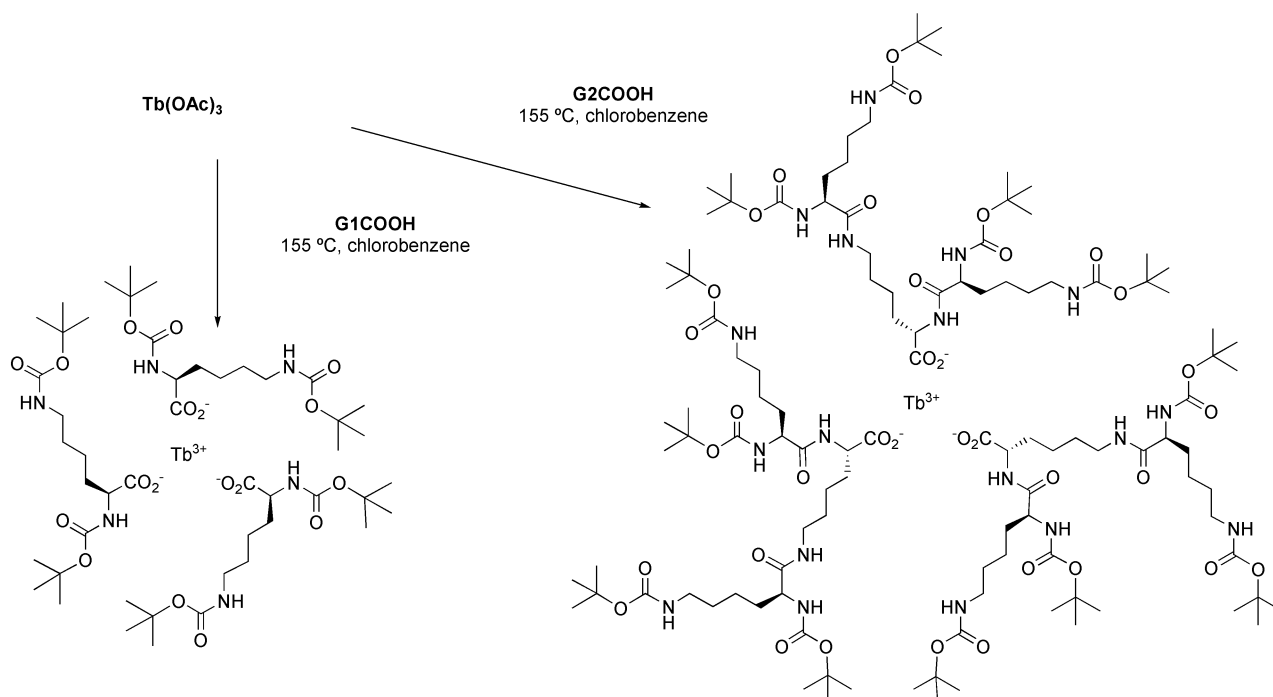
Scheme 1 Synthesis of **G1–Tb** and **G2–Tb** by reaction of dendritic branches based on L-lysine with terbium(III) acetate in chlorobenzene.

acetic acid was removed efficiently and the reaction was stopped after one hour. If the reaction was left too long, or inefficient removal of acetic acid occurred, then deprotection of the Boc groups from the complex became problematic (as illustrated by elemental analysis – see below). It is well-known that Boc groups can be removed either at high temperatures or in the presence of acids.[14] As previously reported, no further purification of the dendritic lanthanide complexes was attempted and they were stored in a desiccator and characterised using a variety of techniques.

Characterisation of complexes G1–Tb and G2–Tb

IR Spectroscopy was performed on KBr discs of the two dendritic lanthanide complexes, and their spectra were compared against those of the original dendrons (Fig. 2). This was important to check that the dendrons were still intact after the rather harsh reaction conditions. The spectra of ligand and complex are broadly similar, indicating that the structure of the ligand remains intact. However, the peak at 1700 cm^{-1} in the spectrum of the ligand is replaced by peaks at 1690 and 1580 cm^{-1} in the complex. This band corresponds to the C=O stretching frequency and suggests that the bonding environment

around C=O has changed. This could correspond to the formation of a lanthanide–carboxylate bond. For **G2–Tb**, once again the structure of the ligand appeared to be intact. Similarly to **G1–Tb**, the strong C=O band (1695 cm^{-1}) was no longer evident. However, specific replacement peaks could not be distinguished owing to the complex fingerprint of the second generation dendritic branches, which possess many C=O groups.

Mass spectrometry was used in an attempt to provide further characterisation of the complexes, and furthermore to ascertain whether the ligands had withstood the harsh reaction conditions. Complex **G1–Tb** did not fly effectively under electrospray conditions, however, **G2–Tb** gave useful spectra. The negatively charged electrospray mass spectrum gave a molecular ion peak at m/z 801, corresponding to the mass of the free ligand $[L - H]^-$. There was also a small peak (<10%) in evidence at m/z 701, corresponding to $[L - Boc - H]^-$. This indicates that only a small amount of ligand deprotection (or mass spectral fragmentation) may have taken place.

The positively charged electrospray mass spectrum from methanolic solution was more complex and useful (Fig. 3). Free ligand was once again apparent at m/z 825, corresponding to
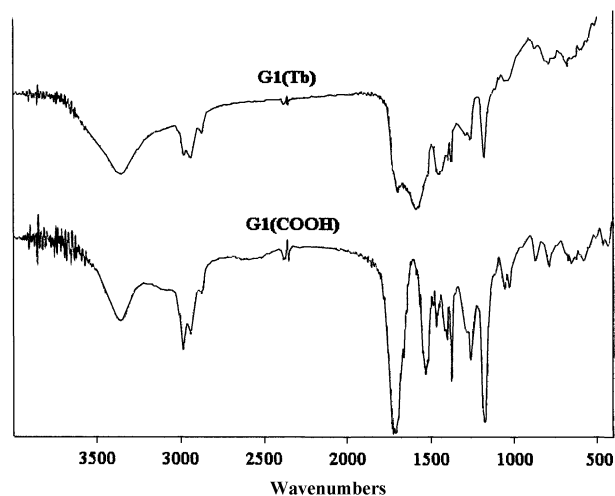

Fig. 2 IR spectra of **G1–Tb and G1(COOH)** measured as KBr discs.
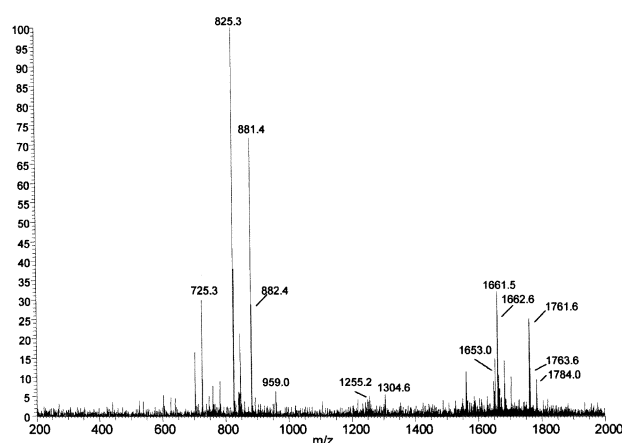

Fig. 3 Positive ion electrospray mass spectrum of **G2–Tb**. The assignments of the peaks to different combinations of ligand and terbium are given in the text and experimental.

[M + Na]+. Interestingly, however, peaks could also be observed for ligand-lanthanide complexes at m/z 1761 [2(L − H) + Tb]+ and m/z 1784 [2(L − H) + Tb + Na]+ and a major peak at m/z 881 could be assigned to a corresponding doubly charged ion, [2(L − H) + Tb + H]2+. Peaks were again observed with 100 mass units less, indicating a small amount of deprotection (or mass spectral fragmentation) of the ligand. A minor peak was also observed at m/z 959, corresponding to [(L − H) + Tb − H]+. The limit of our electrospray detector was m/z 2000, so we were unable to directly detect Tb with three dendritic ligands bound. However, a small doubly charged peak could be observed at m/z 1304, which corresponds to [3(L − H) + Tb + 2Na]2+. This analysis accounts for the majority of peaks observed in the mass spectrum. Although the mass spectral evidence for complex formation in this case is only partial, it is noteworthy that Kawa and Fréchet could not achieve *any* mass spectral characterisation of their complexes [9a] – a factor they assigned to the weakly bound electrostatic complex being readily dissociated under mass spectral ionisation conditions. Our mass spectra on the other hand, provide definite evidence for the occurrence of ligand–lanthanide interactions.

Elemental analysis was an important method for checking the purity of the materials isolated from the reaction. All of the results were within reasonable agreement with calculated values (see Experimental section). However, on one occasion, when the reaction was allowed to heat for 90 min (rather than 60 min), the material obtained had an elemental analysis that was much too high in nitrogen (*ca.* 2%) and much too low in carbon (*ca.* 8%). We accounted for this observation by the deprotection of the Boc groups under the harsh reaction conditions (as described above).

NMR spectrometry was performed on the two complexes. As expected for lanthanide complexes, broad spectra were observed, with some peaks shifted up to 200 ppm downfield. This indicates coordination of the ligand to the paramagnetic lanthanide ion. Due to the broadness of the peaks, it was unfortunately not possible to assign these NMR spectra, but they do provide evidence that ligation has occurred.

Lewis-acid properties of the terbium(III) ions

The Diels–Alder cycloaddition between methylcyclopentadiene and p-benzoquinone is an experiment which illustrates the effect of a Lewis acid on regioselectivity (Scheme 2).[15] In the absence of Lewis acid this reaction, which uses freshly cracked methylcyclopentadiene, is reported to give a product ratio of 45 : 55 (**1** : **2**), whilst in the presence of AlCl3 this ratio changes to 75 : 25 (**1** : **2**) (*i.e.* the formation of product **1** is favoured by electronic effects). The Lewis-acid effect is the result of the coordination of p-benzoquinone to Al3+.
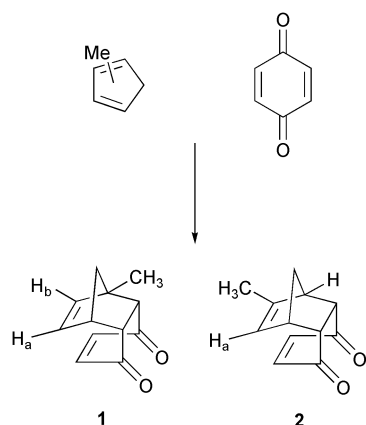
Scheme 2 Diels–Alder reaction between freshly cracked methylcyclopentadiene and p-benzoquinone has two distinct regiochemical outcomes.

Table 1 Outcomes of the Diels–Alder reaction in the presence of different Lewis-acid additives

Reaction additive	Ratio of products **1** : **2**
None (blank)	47 : 53
Tb(OAc)3	50 : 50
G1–Tb	46 : 54
G2–Tb	46 : 54

We chose this simple reaction to investigate the effect of our terbium complexes on the regioselectivity of this reaction. The reaction was performed following the literature methodology,[15] and the effects of **G1–Tb**, **G2–Tb** and Tb(OAc)3 on the product distribution were monitored several times (Table 1). The alkenic protons, H_a and H_b in the product could be differentiated in the NMR spectra of **1** and **2** and this allowed us to determine the relative ratios of compounds **1** and **2**. Disappointingly, however, unlike AlCl3, these complexes had very little effect on the ratios of products observed. It is possible that Tb(OAc)3 had a small effect on the product ratio (towards product **1** – the same direction as AlCl3) but the effect was small, whilst that of the dendritic compounds was zero.

However, an interesting observation came out of this study which gives a significant insight into the Lewis-acid ability of these compounds. When terbium(III) acetate was used as the Lewis acid, the product resonances in the NMR spectrum were significantly broadened (Fig. 4). This indicates that the paramagnetic Lewis acid remains coordinated to the product once the reaction is complete and a minimal work-up has been performed. When **G1–Tb** and **G2–Tb** were used as catalysts, however, the NMR spectra of the product mixture were identical to that for the reaction with no additive present (*i.e.* sharp peaks were observed, Fig. 4). This indicates that the lanthanide ion does not remain bound to the product in these two cases. It is therefore less surprising that these dendritic complexes apparently have no effect on the progress of the reaction.
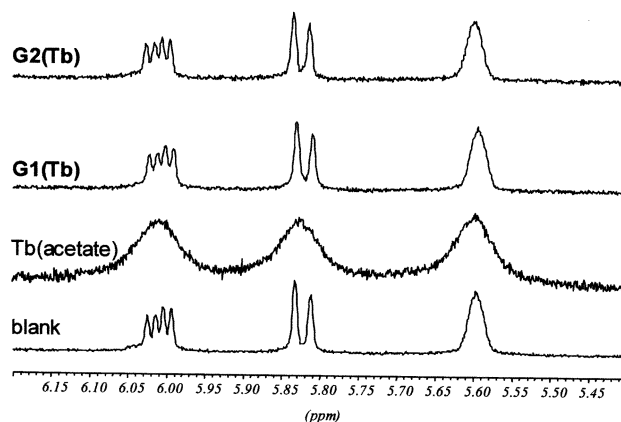
Fig. 4 NMR spectra of mixture of products **1** and **2** from the test reaction, illustrating the effect of terbium acetate in broadening the NMR peaks – indicating that Tb3+ is bound to the Diels–Alder reaction product in this case.

It is interesting to question why these dendritic terbium complexes do not remain bound to the product in the same way that terbium acetate does, and there are two possible explanations for this observation. Firstly, it is possible that the rather large reagents/products are unable to sterically access the vacant coordination sites on the encapsulated lanthanide ion. This is probable for **G2–Tb** but slightly less plausible for **G1–Tb** which only has relatively small ligands. The alternative explanation is that the dendritic branches themselves are able to use their donor atoms (*e.g.* C=O) to fill the vacant coordination sites on the Tb(III). This type of intramolecular complexation would effectively block the vacant sites which are essential for Lewis

acidity and hence prevent interaction of the terbium(III) ion with the C=O of benzoquinone. Interestingly, Kawa and co-workers have recently reported that on increasing the dendritic generation of their dendritic terbium complexes, the co-ordination number of the metal ion increases – with oxygen atoms in the dendritic branches themselves being able to bind to vacant sites on the lanthanide.[9c] Given the flexibility of our lysine based dendritic branches, and the fact that the amide C=O groups of lysine dendrimers are known to bind weakly to lanthanides,[12] the concept of intramolecular ligation preventing binding is quite plausible in this case. This factor will clearly hinder the action of these dendritic complexes as Lewis acids.

Conclusions

This article reports the synthesis and characterisation of novel complexes between terbium(III) ions and dendritic branches based on L-lysine building blocks. The ability of these Lewis-acidic complexes to influence the outcome of a Diels–Alder reaction was investigated, but they were found to have no effect. Interestingly, however, terbium(III) acetate was observed to remain bound to the product of the reaction, broadening its NMR spectrum, whilst the dendritic terbium complexes did not. This indicates that the Lewis-acidic centre may be inaccessible (both to substrate and product) in the more highly functionalised dendritic derivatives.

These results indicate that for effective Lewis-acid catalysis within an encapsulated environment it is highly desirable to ensure that:

(i) sufficient space remains for substrate access – we have recently reported a similar negative steric effect in the development of encapsulated binding sites for anionic guests,[7g]

(ii) there are no donor atoms present within the encapsulating framework which can coordinate to the Lewis acid, hence negating its potential catalytic or reaction-directing effects.

These general principles will be of use for researchers interested in the design of biomimetic encapsulated Lewis-acidic metal ions who wish to ensure that the function of their active centre is not lost on encapsulation.

Experimental

Materials and methods

^{1}H NMR spectra were determined on a Bruker AMX 500 (500 MHz) instrument, and referenced to residual solvent. Solid IR using KBr disks were performed using a Mattson Sirius Research FTIR spectrometer. Electrospray mass spectrometry was carried out on a Finnigan LCQ using methanolic solutions of the complexes. Elemental analyses were performed by the microanalytical lab at The University of Manchester.

Synthesis and characterisation

Dendritic ligands **G1(COOH)** and **G2(COOH)** based on L-lysine were synthesised using literature methodology and had characterisation data in full agreement with those previously reported.[6g]

Complex G1–Tb

Hydrated terbium acetate was dehydrated under a stream of nitrogen at 165 °C for 1 h to give Tb(OAc)$_3$. Tb(OAc)$_3$ (106 mg, 0.315 mmol) was dissolved in chlorobenzene (20 ml) together with **G1(COOH)** (0.33 g, 0.946 mmol). The mixture was refluxed under N$_2$ at 155 °C. A Dean–Stark apparatus was used to continuously remove acetic acid/chlorobenzene from the reaction mixture and fresh chlorobenzene was added. The reaction was stopped after 1 h by evaporation of the solvent under high vacuum. The product was dried overnight under high vacuum and the pale yellow solid produced, **G1–Tb**, was

stored in a vaccum dessicator over CaSO$_4$ (310 mg, 0.26 mmol, 83%).

Yellow solid; v_{max} (KBr disc)/cm^{-1}: 3346m, 2977m, 2933m, 2864w, 1687m, 1577s, 1439m, 1367m, 1254m, 1171m, 1043w; Elemental analysis: C$_{48}$H$_{87}$N$_6$O$_{18}$Tb·H$_2$O requires C, H, N: 47.52, 7.39, 6.93; found: 47.06, 7.10, 7.14%.

Complex G2–Tb

Hydrated terbium acetate was dehydrated under a stream of nitrogen at 165 °C for 1 h to give Tb(OAc)$_3$. Tb(OAc)$_3$ (35 mg, 0.10 mmol) was dissolved in chlorobenzene (20 ml) together with **G1(COOH)** (0.25 g, 0.30 mmol). The mixture was refluxed under N$_2$ at 155 °C. A Dean–Stark apparatus was used to continuously remove acetic acid/chlorobenzene from the reaction mixture and fresh chlorobenzene was added. The reaction was stopped after 1 h by evaporation of the solvent under high vacuum. The product was dried overnight under high vacuum and the pale yellow solid produced, **G1–Tb**, was stored in a vaccum dessicator over CaSO$_4$ (255 mg, 0.099 mmol, 99%).

Yellow glassy solid; v_{max} (KBr disc)/cm^{-1}: 3329s, 2978s, 2933s, 2866m, 1655s, 1523s, 1365s, 1252s, 1165s, 1093s, 1045s, 1020s; Elemental analysis: C$_{114}$H$_{207}$N$_{18}$O$_{36}$Tb·2H$_2$O requires C, H, N: 52.64, 8.18, 9.69; found: 52.28, 7.99, 9.67; m/z (positive ion electrospray, L = **G2(COOH)**) The molecular ion *i.e.* $[3(L - H) + Tb]^+$ requires 2562, found ions with three ligands bound to Tb(III): 1304 $[3(L - H) + Tb + 2Na]^{2+}$ (5%); ions with two ligands bound to Tb(III): 1761 $[2(L - H) + Tb]^+$ (27%), 1784 $[2(L - H) + Tb + Na]^+$ (10%), 881 $[2(L - H) + Tb + H]^{2+}$ (75%), 1662 $[2(L - H) - Boc + Tb + H]^+$; ions with one ligand bound to Tb(III): 959 $[(L - H) + Tb - H]^+$ (7%); ions corresponding to free ligand: 825 $[L + Na]^+$ (100%), 725 $[L - Boc + Na]^+$ (30%).

Diels–Alder reaction

The effect of the terbium complexes on the Diels–Alder reaction between methylcyclopentadiene and *p*-benzoquinone were investigated using the procedure described in ref. 15.

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