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p-tert-Butylcalix[8]arene: An extremely versatile platform for cluster formation**

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calixarenes; cluster compounds; coordination compounds; lanthanides; self-assembly

Abstract

p-tert-Butylcalix[4]arene is a bowl-shaped molecule capable of forming a range of polynuclear metal clusters under different experimental conditions. *p-tert*-Butylcalix[8]arene is a significantly more flexible analog that has previously been shown to form mono- and bi-nuclear lanthanide (Ln) metal complexes. The latter (cluster) motif is commonly observed and involves the calixarene adopting a near double-cone conformation, features of which suggested that it may be exploited as a type of assembly node in the formation of larger polynuclear lanthanide clusters. Variation in the experimental conditions employed for this system provides access to Ln₁, Ln₂, Ln₄, Ln₅, Ln₆, Ln₇ and Ln₈ complexes, with all polymetallic clusters containing the common bi-nuclear lanthanide fragment. Closer inspection of the structures of the polymetallic clusters reveals that all but one (Ln₈) are in fact based on metal octahedra or the building blocks of octahedra, with the identity and size of the final product dependent upon the basicity of the solution and the deprotonation level of the TBC[8] ligand. This demonstrates both the versatility of the ligand towards incorporation of additional metal centers, and the associated implications for tailoring the magnetic properties of the resulting assemblies in which lanthanide centers may be interchanged.

Introduction

Polymetallic *4f* and mixed *3d-4f* clusters hold great potential for device application with respect to single-molecule magnetism and molecular cooling.^[1] One of the major challenges in this area is the systematic design and controlled assembly of clusters with particular coordination modes. The *p-tert*-butylcalix[*n*]arenes (TBC[*n*], where *n* indicates the number of aryl units) are cyclic polyphenols that vary in ring size depending on reaction conditions employed during synthesis.^[2] Given their polyphenolic nature it is somewhat surprising that, until recently, these molecules have received little attention with respect to the construction of large polynuclear metal clusters.^[3] In this regard we (amongst others) have employed TBC[4] as a cluster support with a view to mapping out associated assembly modes and coordination constraints over a range of conditions, as the molecule adopts a bowl-shape both prior to and post complexation of either a transition or lanthanide metal center (TM and Ln, respectively).^[4,5] With TMs we have synthesized and characterized a range of magnetically interesting species that are based around three distinct cluster motifs; Mn^{III}₂Mn^{II}₂TBC[4]₂ Single-Molecule Magnets (SMMs) with a planar diamond or butterfly-like core,^[4b,c] Cu^{II}₉TBC[4]₃ clusters based on tri-capped trigonal prisms that behave as versatile anion receptors,^[4d] and phosphinate-bridged dimers of Mn^{III}Mn^{II}TBC[4] dimers that are structurally related to the aforementioned Mn^{III}₂Mn^{II}₂TBC[4]₂ SMMs.^[4e] We have also incorporated lanthanide metals into *3d* systems to afford “square in a square” Mn^{III}₄Ln^{III}₄TBC[4]₄ clusters that behave as SMMs or magnetic refrigerants depending simply on the Ln employed,^[4f,g] and Fe^{III}₂Ln^{III}₂TBC[4]₂ butterflies that represent an

important second entry point into mixed $3d$ - $4f$ systems.^[4b] Finally we have also carried out reactions involving just lanthanide salts, and have reported the formation of $\text{Ln}^{\text{III}}_6\text{TBC}[4]_2$ clusters in which the metal centers are arranged at the vertices of an octahedron.^[4i]

p-*tert*-Butylcalix[8]arene (TBC[8]) is significantly more flexible than TBC[4] due to annular inversion, and metal complexes^[6] (TM and Ln) formed with this ligand most frequently adopt three particular conformations: pleated-loop,^[6c,e,f,i,j,o,p,l,v] double-cone,^[6a,b,q,s,t,u] and a third in which the molecule wraps around a small cluster in a manner akin to the shell of a tennis ball.^[6d,h,k,l,m,n] With respect to Ln TBC[8] complexes (there are only 10 in total in the Cambridge Structural Database^[7]), one mononuclear complex has been reported in which the calixarene adopts a pleated-loop conformation.^[6o] In this complex the europium center is bound to oxygen atoms of two deprotonated TBC[8] phenol groups, with its coordination sphere being filled by three ligated DMF molecules and one chelating nitrate anion. The remaining nine structures are all dinuclear and all have the TBC[8] in a near-perfect double-cone conformation, are essentially isostructural, and have the general formula $[\text{Ln}^{\text{III}}_2(\text{TBC}[8]-6\text{H})(\text{Solv})_5] \cdot x\text{Solv}$ (where Solv = DMF or DMSO).^[6q,s,t,u] All of these structures have similarity in the arrangement of the ligated solvent molecules; two occupy the cavities presented by the near-perfect double-cone TBC[8], one bridges the two Ln centers beneath the double-cone, and the remaining two are positioned either side of said bridging molecule.

Analysis of the common structural features in our TBC[4]-supported clusters shows that, whether the calixarene binds a TM^{II} (Cu) or TM^{III} (Mn or Fe) metal center, the calixarene cavity is occupied by a ligated solvent molecule. In conjunction with a bound hydroxide ligand beneath the complex, the phenolic O-atoms act as bridges to other Ln or TM centers forming polymetallic $3d$ or $3d$ - $4f$ assemblies (Figure 1A); i.e. the metal-calixarene moiety can be regarded as a “cluster ligand” from which much larger molecules can be self-assembled.^[4b-h] This is also true for Ln^{III} -TBC[4] clusters, although the increased coordination numbers of the lanthanide ions results in a variation in the number of bridging hydroxides present in the resulting assembly, as shown in Figure 1B.^[4i] Similar analysis of the previously reported (and isostructural) $\text{Ln}^{\text{III}}_2\text{TBC}[8]$ complexes described above suggested to us that the solvent occupied coordination sites below the near-perfect double-cone could be used to form larger clusters (e.g. by replacement of the solvent in Figure 1C with multiply-bridging oxo or hydroxo ligands). Here we show that this is indeed the case, and by varying (a) the lanthanide salts employed, (b) the reactant stoichiometries and (c) the solvent systems, all at ambient temperature, it is possible to readily access a series of Ln_1 , Ln_2 , Ln_4 , Ln_5 and Ln_6 complexes. Furthermore the use of high temperature and pressure results in the formation of larger Ln_7 and Ln_8 complexes, depending on the lanthanide employed. In total six of these complexes are new, with five containing the $\text{Ln}^{\text{III}}_2\text{TBC}[8]$ fragment, despite there being significant changes in degrees of deprotonation of the TBC[8] support. A close inspection of the new, polymetallic (Ln_x , with $x \geq 4$)

structures in fact reveals that the metallic skeletons are generally based on octahedra, or the building blocks of octahedra, with complex **2** being a capped triangle, complex **3** a square-based pyramid, complex **4** an octahedron, complex **5** a capped octahedron and complex **6** a gyrobifastigium (8-vertex 26th Johnson solid, a diagonally bi-capped square plane). Although this report focuses solely on structural aspects of the series, the potential to interchange different Ln centers in some of these cluster types will have marked effects on the resulting magnetic properties. These studies will be reported in due course.

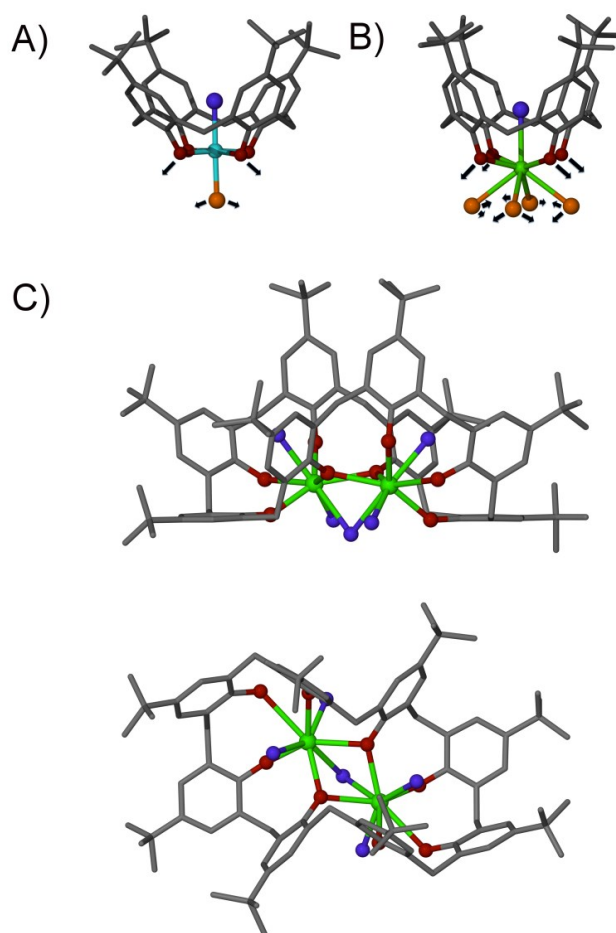
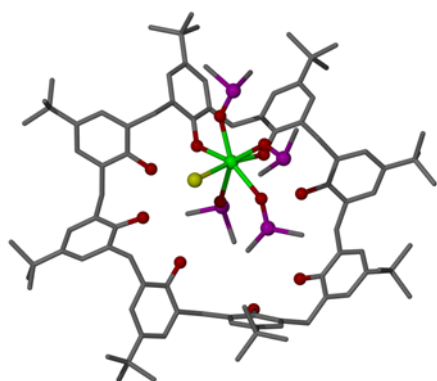


Figure 1. A) Transition metal (TM^{II} or TM^{III}) TBC[4] fragment with ligated solvent and bridging hydroxide groups shown.^[4b] B) Lanthanide metal TBC[4] fragment with oxygen atoms of ligated solvent and bridging hydroxide groups shown as spheres.^[4i] C) Orthogonal views of the commonly observed Ln₂TBC[8] complex with oxygen atoms of ligated solvent molecules (terminal and bridging) shown as spheres.^[6o] Arrows in A) and B) indicate bridging to other metal centers (TM or Ln) from deprotonated lower-rim TBC[4] oxygen atoms or hydroxide groups. Color code: C – grey, O – red, TM – light blue, Ln – green, ligated solvent – mauve, hydroxide O-atom – orange. Hydrogen atoms omitted for clarity, figures not to scale.

Results and Discussion

Through a combinatorial approach we have synthesized and characterized six lanthanide complexes of TBC[8]. The first in the series is a variant of the previously reported $\text{Ln}_1\text{TBC}[8]$ complex^[60] in which the chelating nitrate anion is replaced by a chloride. In a number of our experiments we obtained the same general $[\text{Ln}_2(\text{TBC}[8]-6\text{H})(\text{Solv})_5] \cdot x\text{Solv}$ complex as that shown in Figure 1C, and this will not be discussed further here.^[6q,s,t,u] The remaining five new complexes / clusters formed in our experiments all contain a related $\text{Ln}_2\text{TBC}[8]$ moiety which is in fact a smaller fragment in the construction of frameworks generally based on octahedra, and in which the calixarene adopts either a perfect or near-perfect double-cone conformation. In the case of perfect double-cones this involves a small structural correction to the motif shown in Figure 1C. Various additional ligated solvent molecules are present in the different structures described below, and significant changes in the degree of deprotonation of TBC[8] are evident within the series. A description of general cluster composition is also presented.

[Gd(TBC[8]-2H)Cl(dmsO)₄]·MeCN·H₂O·(dmsO)₂·hex, 1: Reaction of TBC[8] with triethylamine and gadolinium(III) chloride hexahydrate in an acetonitrile / dimethylsulfoxide solution, followed by diffusion with hexane, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in a monoclinic cell and structure solution was carried out in the space group *C2/c*. Analysis of the asymmetric unit in **1** shows that the complex formed is similar to the $\text{Ln}_1\text{TBC}[8]$ complex described in the introduction. The TBC[8] in **1** is in a pleated-loop conformation and exists as a di-anion (Figure 2). The Gd^{III} center is seven coordinate and pentagonal bipyramidal, bonding to the two de-protonated TBC[8] phenol groups, a coordinated chloride anion (Gd...Cl, 2.696 Å) and four ligated DMSO molecules. The Gd...O bond lengths are in the range 2.316-2.410 Å. Overall the structure is unexceptional, but characterization confirms versatility towards the inclusion of different anions in the complex as a whole.



← **Figure 2.** Structure of **1** showing the pleated-loop conformation of TBC[8]. Non-coordinating solvents and hydrogen atoms omitted for clarity. Color code: C – grey, O – red, Gd – green, Cl – yellow, S – purple.

$[\text{Ce}^{\text{IV}}_4(\text{TBC}[8]-6\text{H})_2(\mu_3\text{-O})_2(\text{dmf})_4]\cdot(\text{dmf})_5\cdot\text{hex}\cdot\text{MeCN}$, **2**: Reaction of TBC[8] with triethylamine and cerium(III) nitrate hexahydrate in an acetonitrile / dimethylformamide solution, followed by diffusion with hexane, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in an orthorhombic cell and structure solution was carried out in the space group *Pbca*. The asymmetric unit in **2** comprises the large TBC[8]-supported Ce^{IV}_4 cluster shown in Figure 3 and three ordered DMF of crystallization. In addition to this there is diffuse electron density associated with badly disordered hexane (one molecule), acetonitrile (one molecule) and DMF (two molecules) of crystallization. The four Ce(IV) ions are connected to each other “internally” by two $\mu_3\text{-O}^{2-}$ ions (Ce...O, 2.207-2.302 Å), forming a bowl-shaped or ladder-like $[\text{Ce}^{\text{IV}}_4\text{O}_2]^{12+}$ moiety (Figure 4). This is a commonly observed fragment in TM(III) clusters (*e.g.* in the chemistry of Mn(III) or Fe(III)) and is often referred to as a “butterfly”.^[8] In the context of the present paper and the relationship between complexes **1-7**, however, perhaps the most apt description is that of a capped triangle (*vide infra*). The Ce^{IV} centers are all seven-coordinate and pentagonal bipyramidal in geometry. Each TBC[8] exists as a hexa-anion [there are two intra-molecular H-bonds between neighboring phenolic O-atoms per TBC[8] molecule (*e.g.* O13...O14 and O17...O18 ~2.5 Å)] and bridges three Ce^{IV} ions (Ce1, Ce3, Ce4 or Ce2, Ce3, Ce4) across one complete side of the butterfly. Ligated DMF molecules occupy the cavities generated by each of the TBC[8] molecules in **2**, adopting the double-cone conformation. In this arrangement each TBC[8] is reminiscent of two TBC[4]s and the ligated DMF molecules form intra-molecular interactions with the aromatic rings of the calixarene (symmetry unique $\text{CH}\cdots\pi$ interactions with $\text{CH}\cdots$ aromatic centroid distances of ~3.5 Å).

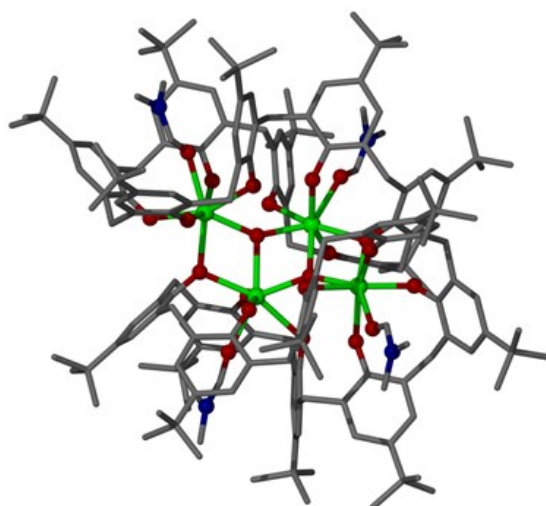


Figure 3. Expanded structure in **2** showing two $\text{Ln}^{\text{III}}_2\text{TBC}[8]$ fragments linked by $\mu_3\text{-O}^{2-}$ ions. The calixarenes are in the double cone conformation akin to that shown in Figure 1C. Color code: C – grey, O – red, N – Blue, Ce – green.

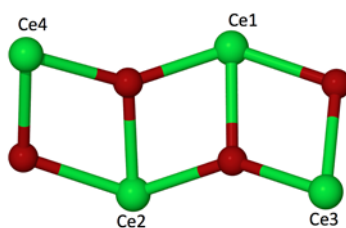


Figure 4. The poly-metallic ladder-like core found in the structure of **2**.

[Tb^{III}₅(TBC[8]-5H)(μ_4 -O)(μ_3 -OH)₄Cl(dmsO)₈(H₂O)₃]Cl₃ · (dmsO)₂(hex)₂, **3:** Reaction of TBC[8] with triethylamine and terbium(III) chloride hexahydrate in an acetonitrile / dimethylsulfoxide solution, followed by diffusion with hexane, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in a triclinic cell and structure solution was carried out in the space group *P*-1. The asymmetric unit in **3** comprises half of the complex shown in Figure 5, two ordered DMSO of crystallization, and diffuse electron density associated with two hexane molecules of crystallization. The metallic skeleton (Figures 5 and 6) of complex **3** describes a distorted square-based pyramid with Tb1-Tb4 in the square base and Tb5 on the apex. Tb1-Tb4 are connected to each other *via* one μ_4 -O²⁻ ion in the basal plane (O11) and to Tb5 *via* four μ_3 -OH⁻ ions, one on each triangular face of the pyramid (O12-O15); the core of the complex is thus [Tb^{III}₅(μ_4 -O)(μ_3 -OH)₄]⁹⁺. The Tb^{III} ions are all eight coordinate and in square antiprismatic geometries, although those in the basal plane are more distorted. All have [LnO₈] coordination spheres with the exception of Tb2 which is bonded to the sole coordinated Cl⁻ anion. The TBC[8] ligand is penta-ionic with the three protonated arms each H-bonding to one Cl⁻ counter anion (~3 Å). The latter are also H-bonded to the terminally bonded H₂O molecules. The TBC[8] molecule adopts the double cone conformation (Figure 5), bridging the four Tb ions in the square base of the pyramid. The coordination sites of the metal ions are completed by the presence of several terminally bonded solvent molecules (DMSO and H₂O), with the ligated DMSO molecules occupying the cavities generated by each of the TBC[8] molecules, with CH \cdots aromatic centroid distances of ~3.5 Å. Interestingly Tb5 – the apical metal ion – is not coordinated to the calixarene ligand at all, being connected to the rest of the molecule only through the four μ_3 -OH⁻ ions. Its exterior square face is entirely comprised of terminally ligated solvent, suggesting the possibility of further cluster growth by solvent substitution.

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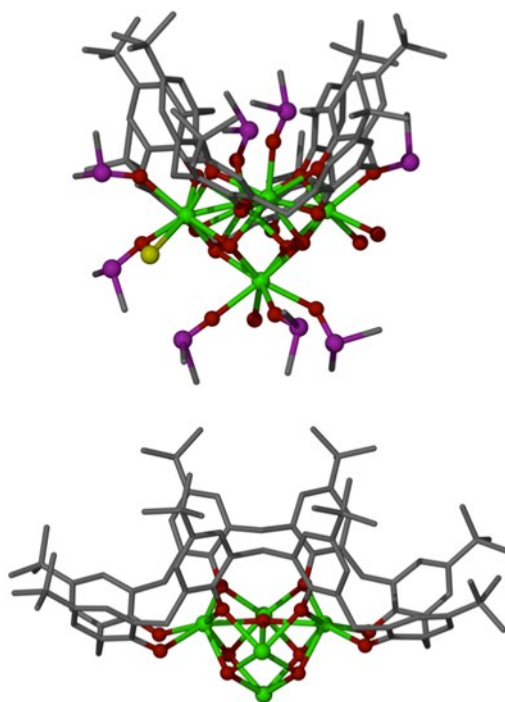


Figure 5. Two views of the structure of **3** showing the double-cone conformation of TBC[8] akin to that shown in Figure 1C. Non-coordinating solvents omitted in bottom view for clarity, and hydrogen atoms omitted in both. Color code: C – grey, O – red, N – Blue, Tb – green, S – purple.

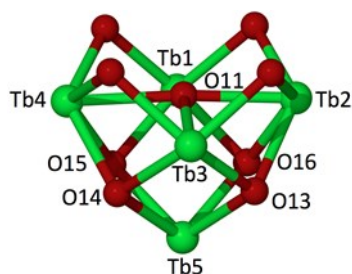


Figure 6. Square pyramidal cluster core found in the structure of **3** showing incorporated $\mu_4\text{-O}^{2-}$ and $\mu_3\text{-OH}^-$ ions.

$[\text{Ce}^{\text{IV}}_6(\text{TBC}[8]-6\text{H})_2(\mu_4\text{-O})_2(\mu_2\text{-OMe})_4(\mu_2\text{-O})_2(\text{dmf})_4] \cdot (\text{dmf})_6 \cdot \text{hex}$, **4**: Reaction of TBC[8] with triethylamine, cerium(III) nitrate hexahydrate and ammonium perchlorate in a methanol / dimethylformamide solution, followed by diffusion with hexane, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in a triclinic cell and structure solution was carried out in the space group $P\bar{1}$. The asymmetric unit in **4** comprises half of the cluster shown in Figure 7, two ordered DMF of crystallization, and diffuse electron density associated

with DMF (1 molecule) and hexane (1 molecule) of crystallization. The metallic skeleton of complex **4** (Figures 7 and 8) is a $[\text{Ce}^{\text{IV}}_6]$ (squashed) octahedron, with Ce1 and symmetry equivalent (s.e.) sitting on the apical sites and Ce2, Ce3 and s. e. occupying the square plane. The latter is slightly asymmetric and is more rectangular than square with two Ce...Ce distances of the order of 4.7 Å and two being approximately 0.5 Å shorter. The distance between the apical site and the four ions in the rectangular plane is ~ 3.3 Å. All six Ce ions are eight coordinate and in square antiprismatic geometries. The apical sites are connected to the four ions in the square plane (and to each other) *via* two $\mu_4\text{-O}^{2-}$ ions (O12 and s.e.), four μ -methoxides (O13, O14 and s.e.) and four phenolic μ -O-atoms from the calixarene ligands (O6, O7 and s.e.). The remaining two, near linear, $\mu\text{-O}^{2-}$ ions (O11 and s.e.) link neighboring Ce(IV) ions across the “short” edges of the rectangle, completing the $[\text{Ce}^{\text{IV}}_6(\mu_4\text{-O})_2(\mu\text{-O})_2(\mu\text{-OMe})_4]^{12+}$ core. Each TBC[8] exists as a hexa-anion [there is one intra-ligand H-bond between neighboring phenolic O-atoms per TBC[8] molecule (O2...O3, ~ 2.55 Å) and one inter-ligand H-bond (O13...O14, ~ 2.45 Å)] and bridges three Ce ions (Ce1-3) across one triangular face of the octahedron. The calixarenes again adopt the double cone conformation with ligated DMF molecules occupying the cavities in a manner identical to that seen for complexes **2** and **3** (Figure 7).

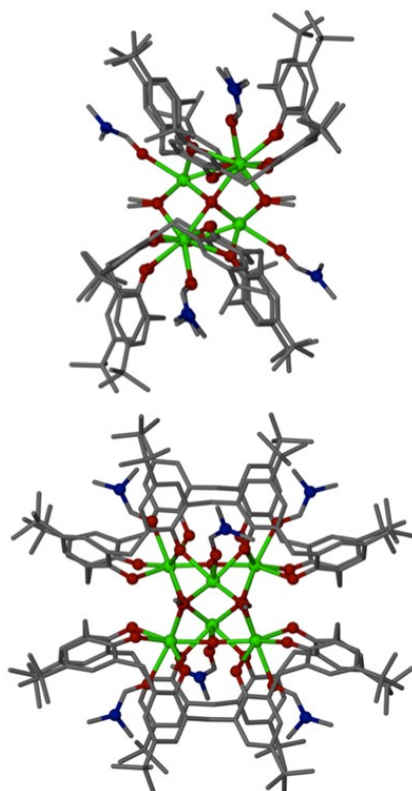


Figure 7. Two views of the structure of **4** showing the double-cone conformation of TBC[8] akin to that in Figure 1C and the metal octahedron. Non-coordinating solvents omitted in bottom view for clarity, and hydrogen atoms omitted in both. Color code: C – grey, O – red, Ce – green, N - blue.

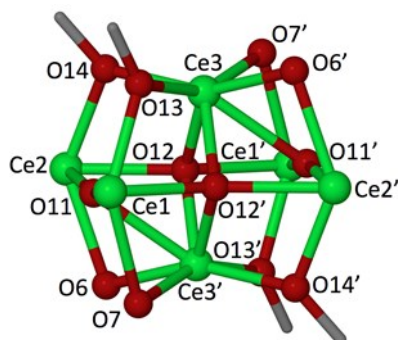


Figure 8. The octahedral cluster core found in the structure of **4** showing incorporated MeO^- and $\mu_4\text{-O}^{2-}$ ions.

[Dy₇(TBC[8]-7H)(TBC[8]-6H)($\mu_4\text{-O}$)₂($\mu_3\text{-OH}$)₂($\mu_2\text{-OH}$)₂(dmf)₉](dmf)₃, **5:** Solvothermal reaction of TBC[8] with triethylamine and dysprosium(III) chloride hexahydrate in a dimethylformamide / methanol solution, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in a triclinic cell and structure solution was carried out in the space group $P\bar{1}$. The asymmetric unit in **5** comprises the cluster shown in Figure 9 and three DMF of crystallization. The metallic skeleton of **5** (Figures 9 and 10) is a rather unusual and distorted capped octahedron: Dy4 and Dy5 occupy the apical sites, Dy1, Dy2, Dy6 and Dy7 occupy the square plane and Dy3 caps the triangular Dy5, Dy6, Dy7 face. In fact Dy3 does not sit directly in the center of this face, being skewed closer to the Dy6-Dy7 vector and thus an alternative description is that of Dy3 being edge-capping rather than face-capping. The central cavity of the octahedron is again filled by two $\mu_4\text{-O}^{2-}$ ions (O31, O32). The edge-capping Dy ion (Dy3) is connected to the octahedron through a combination of two $\mu_3\text{-OH}^-$ ions (O28, O29) and one $\mu\text{-OH}^-$ ion (O30). The remaining hydroxide ion (O33) bridges Dy1 and Dy2 in the square plane. The metal-oxygen core is therefore the asymmetric $[\text{Dy}^{\text{III}}_7(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\mu\text{-OH})_2]^{13+}$.

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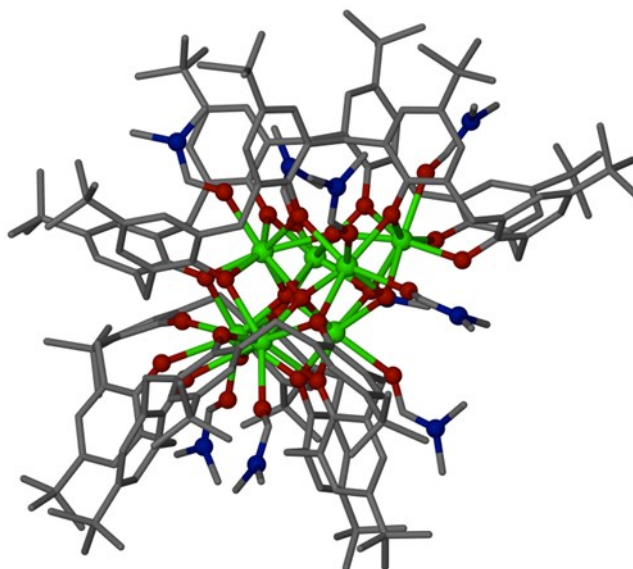


Figure 9. Structure of **5** showing the double-cone conformation of TBC[8]. Non-coordinating solvents and hydrogen atoms omitted for clarity. Colour code: C – grey, O – red, Dy – green, N - blue.

The two TBC[8] ligands are present in different levels of protonation, one being TBC[8]-7H and the other TBC[8]-6H. In the 7- ligand the one remaining proton is shared between neighbors O15 and O16 which are both terminally coordinated (Dy3...O16, 2.532 Å; Dy7...O15, 2.333 Å) and H-bonding to each other (O15...O16, 2.570 Å). For the 6- ligand, the protonated arms are O2 and O3, both being bonded terminally with Dy...O distances of 2.48 Å and 2.821 Å, respectively. Both calixarene ligands adopt the double cone conformation, the 7- ligand bridging a total of six Dy ions and the 6- ligand bridging a total of five Dy ions. The Dy ions are of two types: Dy1, Dy2, Dy4, Dy5, Dy8 are eight coordinate and in square anti-prismatic geometries, whilst Dy3, Dy6 and Dy7 are seven coordinate and pentagonal bipyramidal. The remaining metal coordination sites are again filled with terminally bonded solvent molecules (Figure 9).

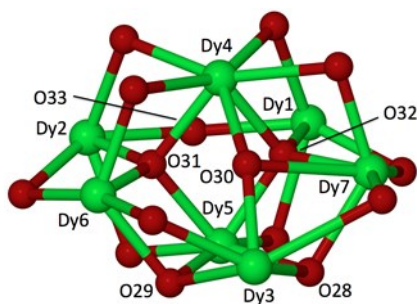


Figure 10. The capped octahedral cluster core found in the structure of **5** showing incorporated $\mu_4\text{-O}^{2-}$ and $\mu_3\text{-OH}^-$ ions.

[Gd₈(TBC[8]-7H)₂(μ₄-CO₃)₂(μ₅-CO₃)₂(μ₂-HCO₂)₂(dmf)₈], **6**: Solvothermal reaction of TBC[8] with triethylamine and gadolinium(III) chloride hexahydrate in a dimethylformamide / methanol solution, afforded large colorless single crystals that were suitable for X-ray diffraction studies. The crystals are in a triclinic cell and structure solution was carried out in the space group *P*1. As the structure was solved in *P*1, the asymmetric unit in **6** comprises the entire cluster shown in Figure 11. The cluster core is disordered over two positions, but for clarity only one will be discussed and shown below. The metallic skeleton of **6** (Figures 11 and 12) is very unusual and conforms to the 26th Johnson solid, the gyrobifastigium. This 8-vertex polyhedron is composed of four squares and four triangles constructed around a central square plane, which in one of the two aforementioned positions is defined by Gd1 – Gd4. On one side the square is bi-capped by Gd5 and Gd6, and on the other Gd7 and Gd8. One μ₄-CO₃²⁻ ion links Gd1 and Gd3 to Gd5 and Gd6, while another on the other side of the cluster links Gd2 and Gd4 to Gd5 and Gd6. One μ₅-CO₃²⁻ ion links Gd7 and Gd8 to Gd1, Gd4 and Gd5, while another on the other side of the cluster links Gd7 and Gd8 to Gd2, Gd3 and Gd6. Gd7 and Gd8 are also doubly linked to one another by two syn, syn μ-formate ligands as shown in Figure 12. The origin of the carbonate ligands is atmospheric CO₂ (in the presence of strong base) and the formate from the breakdown of the DMF solvent under the high temperature, high pressure (solvothermal) reaction conditions. Both are commonly observed occurrences. Attempts to repeat the synthesis through the deliberate addition of CO₃²⁻ / formate have thus far failed. The metal oxygen core is therefore [Gd^{III}₈(μ₄-CO₃)₂(μ₅-CO₃)₂(μ₂-HCO₂)₂]¹⁴⁺.

The two TBC[8] ligands are both present at the same level of deprotonation, that being TBC[8]-7H. The proton is shared between neighbors O5 and O6, and O9 and O16, all of which are terminally coordinated and H-bonding to each other (O5...O6, 2.735 Å; O9...O16, 2.797 Å). Both calixarenes are in the double-cone conformation and both bridge five gadolinium centers. The Gd(III) ions themselves are all 7-coordinate and in pentagonal bipyramidal geometry.

It is interesting to note that complex **6** contains no oxide or hydroxide ions, in contrast to all the other polynuclear Ln cages reported herein. Thus it seems clear, that CO₃²⁻ ions produced *in situ* have acted as their “replacement” sitting in the centre of the cluster and acting as structure-directing or templating anions. This perhaps suggests an alternative synthetic strategy for the successful construction of large polynuclear Ln cluster compounds – the deliberate use of carbonate as a primary bridging ligand.

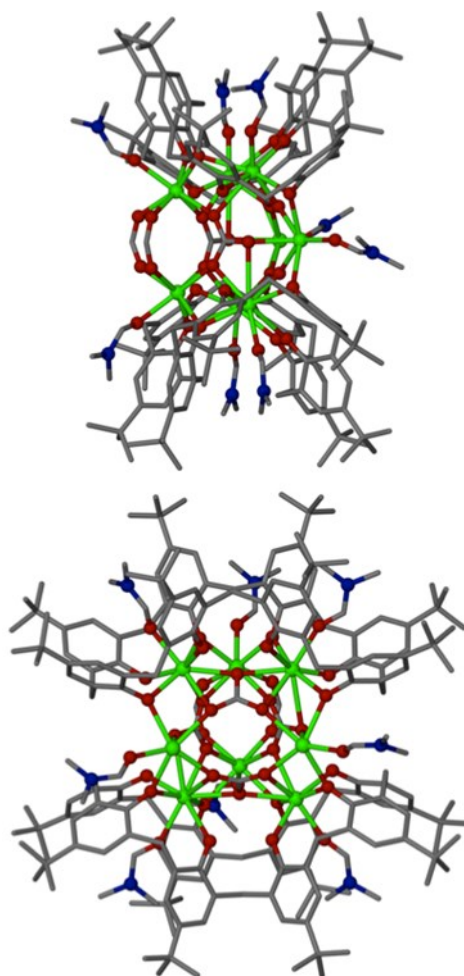


Figure 11. Structure of **6** showing the double-cone conformation of TBC[8] and the asymmetric metal-oxygen core. Hydrogen atoms omitted for clarity. Colour code: C – grey, O – red, Gd – green, N - blue.

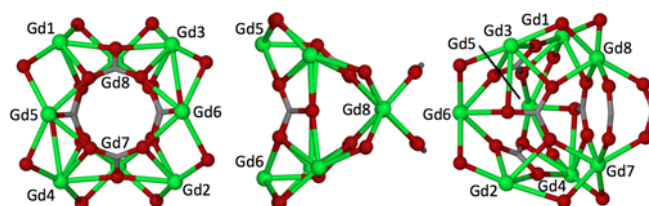


Figure 12. Three views of the gyrobifastigium cluster core found in the structure of **6** showing the incorporated CO_3^{2-} and HCO_2^- ions.

Cluster Construction Analysis

At first, from a quick inspection of Figures 3-12, there appears to be little or no resemblance between

complexes **2-6**. However, upon closer inspection a clear trend emerges: all the structures are based on octahedra or the building blocks of octahedra. Complex **2** is a capped triangle, complex **3** is a square-based pyramid, complex **4** an octahedron and complex **5** a capped octahedron (Figure 13). The variation in structure type must therefore originate from changes in reaction conditions and in the identity of the metal center and its oxidation state. The synthetic methodologies are all very similar (see experimental section), and there are some obvious conclusions to be drawn from these experimental details. The reactions that produce complexes **2** and **4** are analogous, the major difference being the change in solvent from MeCN in the former to MeOH in the latter. This introduces MeO⁻ ions into the reaction mixture and indeed four are incorporated into the crystallized product, each bridging across one vertex of the octahedron. In other words the methoxide ions promote a structural transformation from a capped triangle to an octahedron. In essence this is a simple dimerization.

The reactions which produce complexes **3** ([Tb^{III}₅]) and **5** ([Dy^{III}₇]) are also analogous and, assuming the small change in size of the Ln has no effect, the major difference here is the ratio of ligand:base used in the reaction [1:9 in the former and 1:24 in the latter] and the use of higher temperature and pressure (solvothermal reaction). In complex **3** both ligands are TBC[8]-6H, while in **5** one ligand is TBC[8]-6H and the other TBC[8]-7H, and it is this additional phenolate arm that bridges to the “extra” capping Dy ion. The octahedron observed in **5** is very similar to that formed with TBC[4], suggesting that this may be a favorable construction core for any calixarene containing multiple equivalents of the bowl-shaped tetramer (e.g. TBC[8], TBC[12] and so on).^[4i]

Complex **6** is synthesised from an analogous reaction to that used to produce **5**, but with Gd in place of Dy. This is the only structure in the series that deviates markedly from the octahedral construction core shown in Figure 13. Although this is the case the central square plane of the octahedron is evident, with diagonal bi-capping to afford the gyrobifastigium (the 26th Johnson solid). This 8-vertex polyhedron is composed of four squares and four triangles and is persistently formed experimentally with Gd ions. Although further work will be required to fully elucidate why a different structural motif is being formed, we propose that it is likely that the presence of the centrally templating carbonate ions, and/or a threshold in the lanthanide ion size is responsible. The former clearly have a different coordination mode (μ_4 and μ_5) than oxide or hydroxide ions and thus direct the formation of a different metallic skeleton around which the calixarene must wrap. The latter, often referred to as the “Gd-break” simply reflects the larger coordination numbers often observed for the early, larger lanthanides.^[9] Given the coordination number of the Gd(III) ions in **6** however, the effect/presence of the carbonate anions seems a more plausible explanation. In addition, complex **6** is the only structure in which both cluster supports are TBC[8]-7H. This may therefore suggest that the use of high temperature, high pressure reactions is a route toward achieving full, or nearly full, deprotonation of

the calixarene. In order to conclusively prove this theory we will undertake an expansive combinatorial study of Ln salts, bases (including equivalents used) and solvents employed in cluster formation in a range of temperature and pressure conditions. These findings will be reported in due course.

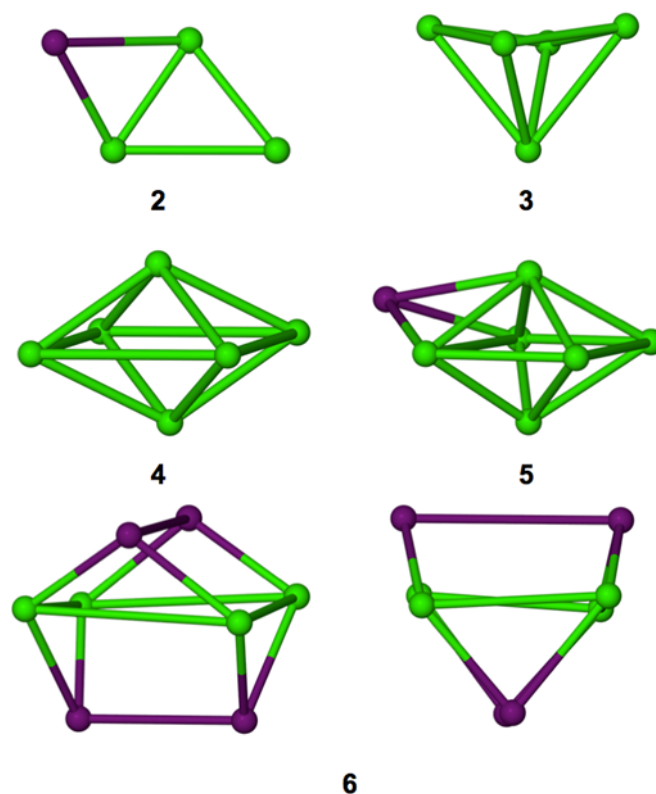


Figure 13. Structure analyses of 2 – 6 showing the common octahedral character (green spheres, squares and triangles) associated with each system. Capping lanthanide vertices are shown in purple. Two orthogonal views are shown for 6 to emphasize the diagonal bi-capping found in the gyrobifastigium polyhedron.

Conclusions

p-tert-Butylcalix[8]arene has previously been investigated as a support for the formation of small (dinuclear) lanthanide(III) clusters. Our investigations into the use of different experimental conditions and lanthanide metals show that this ligand is in fact extremely versatile in terms of both conformation, varying degrees of deprotonation and bridging capacity. This has marked consequences on the resulting ability of the ligand to form a wide range of complexes with cluster motifs containing 2, 4, 5, 6, 7, and 8 lanthanide centers. There are only a small number of reports outlining the use of

other large TBC[*n*]s as cluster supports. The results reported here suggest that an enormous range of alternative and possibly larger clusters may be formed with these supports. Future work will therefore focus on exploring analogous chemistry with the entire family of large TBC[*n*]s (where *n* = 5 – 20). This may show a) that other large TBC[*n*]s display trends in both conformation and level of deprotonation, b) that multiple clusters form simultaneously in solution or c) that particular clusters form selectively under varied experimental conditions. Control over crystallization and experiment will be key in the isolation of specific cluster types with particular lanthanide metals.

With respect to the Ln / TBC[8] clusters reported here, mixed 3*d*-4*f* systems are also under investigation, and the experimental and theoretical investigation of the magnetic properties of **1**, **3**, **5** and **6**, which are non-trivial, will be reported in detail elsewhere.

Experimental Section

All chemicals were purchased from Aldrich and used as supplied. Solvents were not dried prior to use in experiments.

General crystallographic details: Data for **5** was collected on a Bruker Apex II diffractometer operating with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K. Data for complexes **1** - **4**, **6** was collected on a Bruker Apex II CCD Diffractometer at 100(2) K with synchrotron radiation ($\lambda = 0.77490 \text{ \AA}$). CCDC 892672 – 892677 contain the crystallographic information for **1** – **6** respectively.

Synthesis of [Gd(TBC[8]-2H)Cl(dmsO)₄]·MeCN·H₂O·(dmsO)₂·hex, **1:** GdCl₃·6H₂O (0.19g, 0.5 mmol) and TBC8 (0.2g, 0.17 mmol) were dissolved in a mixture of acetonitrile (10 cm³) and dimethylsulfoxide (10 cm³). After 5 minutes of stirring, NEt₃ (2 ml, 1.5 mmol) was added, leaving the solution stirring for a further 2 h. Colorless single crystals suitable for diffraction studies were obtained by diffusion of hexane over a period of 2 weeks. Elemental analysis (%) calculated (found) for C₁₀₈H₁₆₅ClGdNO₁₅S₆, (2102.47): C 61.70 (61.90), H 7.91 (7.95), N 0.67 (0.64). These values are consistent with solvent loss in this system. **Crystal data for 1:** C₁₀₈H₁₆₅ClGdNO₁₅S₆, *M* = 2102.47, Colourless Block, 0.40 · 0.35 · 0.32 mm³, monoclinic, space group *C2/c* (No. 15), *a* = 48.4925(16), *b* = 16.1936(6), *c* = 36.839(2) Å, $\beta = 126.308(2)^\circ$, *V* = 23311.9(17) Å³, *Z* = 8, $2\theta_{\max} = 64.4^\circ$, 124801 reflections collected, 31525 unique (*R*_{int} = 0.0545). Final *Goof* = 1.037, *RI* = 0.0668, *wR2* = 0.1754, *R* indices based on 22746 reflections with *I* > 2σ(*I*) (refinement on *F*²).

Synthesis of [Ce^{IV}₄(TBC[8]-6H)₂(μ₃-O)₂(dmf)₄]·(dmf)₅·hex·MeCN, **2:** Ce(NO₃)₃·6H₂O (0.217 g, 0.5 mmol) and TBC8 (0.2g, 0.17 mmol) were dissolved in a mixture of acetonitrile (10 cm³) and dimethylformamide (10 cm³). After 5 minutes of stirring, NEt₃ (2 ml, 1.5 mmol) was added, leaving the solution stirring for a further 2 h. Colorless single crystals suitable for diffraction studies were

obtained by diffusion of hexane over a period of 2 weeks. Elemental analysis (%) calculated (found) for $C_{211}H_{292}Ce_4N_{10}O_{27}$ (3961.03): C 63.98 (63.75), H 7.43 (7.21), N 3.54 (3.37). **Crystal data for 2:**

$C_{211}H_{292}Ce_4N_{10}O_{27}$, $M = 3961.03$, Brown Block, $0.30 \cdot 0.25 \cdot 0.20 \text{ mm}^3$, orthorhombic, space group *Pbca* (No. 61), $a = 32.0523(13)$, $b = 20.0131(8)$, $c = 68.846(3) \text{ \AA}$, $V = 44162(3) \text{ \AA}^3$, $Z = 8$, $2\theta_{\text{max}} = 58.0^\circ$, 360636 reflections collected, 45081 unique ($R_{\text{int}} = 0.0867$). Final $Goof = 1.188$, $RI = 0.0637$, $wR2 = 0.1693$, R indices based on 35874 reflections with $I > 2\sigma(I)$ (refinement on F^2).

Synthesis of $[Tb^{III}_5(TBC[8]-5H)(\mu_4-O)(\mu_3-OH)_4Cl(dmsO)_8(H_2O)_3]Cl_3 \cdot (dmsO)_2 \cdot (hex)_2$, 3:

$TbCl_3 \cdot 6H_2O$ (0.187g 0.5 mmol) and TBC8 (0.2g, 0.17 mmol) were dissolved in a mixture of acetonitrile (10 cm^3) and dimethylsulfoxide (10 cm^3). After 5 minutes of stirring, NEt_3 (2 ml, 1.5 mmol) was added, leaving the solution stirring for a further 2 h. Colorless single crystals suitable for diffraction studies were obtained by diffusion of hexane over a period of 2 weeks. Elemental analysis (%) calculated (found) for $C_{120}H_{205}Cl_4O_{26}S_{10}Tb_5$ (3320.84): C 43.40 (43.26), H 6.22 (6.27). **Crystal data for 3:** $C_{120}H_{205}Cl_4O_{26}S_{10}Tb_5$, $M = 3320.84$, Colourless Block, $0.30 \cdot 0.20 \cdot 0.18 \text{ mm}^3$, triclinic, space group *P-1* (No. 2), $a = 16.0139(7)$, $b = 21.3862(9)$, $c = 23.1190(10) \text{ \AA}$, $\alpha = 103.392(2)$, $\beta = 99.438(2)$, $\gamma = 103.357(2)^\circ$, $V = 7293.5(5) \text{ \AA}^3$, $Z = 2$, $2\theta_{\text{max}} = 67.2^\circ$, 107739 reflections collected, 43735 unique ($R_{\text{int}} = 0.0508$). Final $Goof = 1.094$, $RI = 0.0416$, $wR2 = 0.1143$, R indices based on 35996 reflections with $I > 2\sigma(I)$ (refinement on F^2).

Synthesis of $[Ce^{IV}_6(TBC[8]-6H)_2(\mu_4-O)_2(\mu_2-OMe)_4(\mu_3-O)_2(dmf)_4] \cdot (dmf)_6 \cdot hex$, 4: $Ce(NO_3)_3 \cdot 6H_2O$ (0.217 g, 0.5 mmol), TBC8 (0.2g, 0.17 mmol) and NH_4ClO_4 (0.06 g, 0.5 mmol) were dissolved in a mixture of methanol (10 cm^3) and dimethylformamide (10 cm^3). After 5 minutes of stirring, NEt_3 (2 ml, 1.5 mmol) was added, leaving the solution stirring for a further 2 h. Colorless single crystals suitable for diffraction studies were obtained by diffusion of hexane over a period of 2 weeks.

Elemental analysis (%) calculated (found) for $C_{216}H_{308}Ce_6N_{10}O_{34}$ (4429.44): C 58.57 (58.81), H 7.01 (7.26), N 3.16 (3.30). **Crystal data for 4:** $C_{216}H_{308}Ce_6N_{10}O_{34}$, $M = 4429.44$, Brown Block, $0.40 \cdot 0.30 \cdot 0.28 \text{ mm}^3$, triclinic, space group *P-1* (No. 2), $a = 16.3625(7)$, $b = 18.4212(7)$, $c = 21.2603(8) \text{ \AA}$, $\alpha = 68.652(2)$, $\beta = 68.475(2)$, $\gamma = 87.483(2)^\circ$, $V = 5522.5(4) \text{ \AA}^3$, $Z = 1$, $2\theta_{\text{max}} = 67.3^\circ$, 82245 reflections collected, 33205 unique ($R_{\text{int}} = 0.0684$). Final $Goof = 0.914$, $RI = 0.0497$, $wR2 = 0.1112$, R indices based on 21735 reflections with $I > 2\sigma(I)$ (refinement on F^2).

Synthesis of $[Dy_7(TBC[8]-7H)(TBC[8]-6H)(\mu_4-O)_2(\mu_3-OH)_2(\mu_2-OH)_2(dmf)_9] \cdot (dmf)_3$, 5:

$DyCl_3 \cdot 6H_2O$ (282 mg, 0.750 mmol) and TBC8 (324 mg, 0.250 mmol) were dissolved in a mixture of dimethylformamide (DMF) (10 cm^3) and MeOH (10 cm^3). After 5 minutes of stirring, NEt_3 (0.83 ml, 6 mmol) was added and the solution stirred for a further 5 minutes. After filtration the solution was placed in Teflon-lined "bomb" and heated to 130°C for 24 hours. Colorless single crystals suitable for diffraction studies were obtained in good yield (91%) after cooling the mixture to room temperature.

Elemental analysis (%) calculated (found) for $C_{212}H_{309}Dy_7N_{12}O_{34}$ (4707.28): C 54.09 (54.39), H 6.62 (6.43), N 3.57 (3.24).

Crystal data for 5: $C_{212}H_{299}Dy_7N_{12}O_{34}$, $M = 4697.13$, Colourless Block, $0.35 \cdot 0.30 \cdot 0.25 \text{ mm}^3$, triclinic, space group $P-1$ (No. 2), $a = 18.9410(11)$, $b = 20.9821(12)$, $c = 29.8973(18) \text{ \AA}$, $\alpha = 81.769(2)$, $\beta = 86.493(2)$, $\gamma = 67.470(2)^\circ$, $V = 10861.7(11) \text{ \AA}^3$, $Z = 2$, $2\theta_{\text{max}} = 46.5^\circ$, 134390 reflections collected, 30891 unique ($R_{\text{int}} = 0.1137$). Final $Goof = 1.000$, $RI = 0.0543$, $wR2 = 0.1044$, R indices based on 18046 reflections with $I > 2\sigma(I)$ (refinement on F^2).

Synthesis of $[Gd_8(TBC[8]-7H)_2(\mu_4-CO_3)_2(\mu_5-CO_3)_2(\mu_2-HCO_2)_2(dmof)_8]$, 6: $GdCl_3 \cdot 6H_2O$ (279 mg, 0.750 mmol) and TBC8 (324 mg, 0.250 mmol) were dissolved in a mixture of dimethylformamide (DMF) (10 cm^3) and MeOH (10 cm^3). After 5 minutes of stirring, NEt_3 (0.83 ml, 6 mmol) was added and the solution stirred for a further 5 minutes. After filtration the solution was placed in Teflon-lined “bomb” and heated to 130°C for 24 hours. Colorless single crystals suitable for diffraction studies were obtained in good yield (78 %). Elemental analysis (%) calculated (found) for $C_{206}H_{280}Gd_8N_8O_{40}$ (4766.46): C 51.91 (52.26), H 5.92 (6.13), N 2.35 (2.61). **Crystal data for 6:** $C_{206}H_{268}Gd_8N_8O_{40}$, $M = 4754.28$, colourless block, $0.09 \cdot 0.05 \cdot 0.04 \text{ mm}^3$, triclinic, space group $P1$ (No. 1), $a = 17.1307(7)$, $b = 20.6804(8)$, $c = 21.0289(13) \text{ \AA}$, $\alpha = 107.905(3)$, $\beta = 105.883(3)$, $\gamma = 109.705(2)^\circ$, $V = 6053.0(5) \text{ \AA}^3$, $Z = 1$, $2\theta_{\text{max}} = 73.5^\circ$, 219323 reflections collected, 89956 unique ($R_{\text{int}} = 0.0374$). Final $Goof = 1.030$, $RI = 0.0750$, $wR2 = 0.2149$, R indices based on 69439 reflections with $I > 2(I)$ (refinement on F^2).

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- [7] Correct as of 14/07/12.

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