Calix[4]arene-supported rare earth octahedra

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A series of calix[4]arene-supported Ln^{III}_6 clusters have been synthesised under facile bench top conditions. The magnetic and structural properties of these clusters are reported, the latter suggesting that the Ln^{III}-calix[4]arene moiety may be
10 used for the construction of other assemblies in a manner akin to that for the Mn^{III}-calix[4]arene analogue.

p-tert-Butylcalix[4]arene (TBC[4]) is a readily accessible bowl-shaped molecule composed of four phenol units linked by methylene bridges.[1] The poly-phenolic nature of this ligand
15 presents it as an excellent candidate for the complexation of transition or lanthanide metal centres (TM and Ln respectively) at what is termed the lower-rim. Despite this feature, methylene bridged calix[4]arenes, unlike their thia and sulfonyl bridged analogues,[2] have received relatively little attention in the context
20 of constructing polynuclear metal clusters.[3,4] In this regard we have recently begun to map out TM and 3d-4f cluster motifs formed with TBC[4] under facile bench top conditions. We first used TBC[4] to synthesise $Mn^{III}_2Mn^{II}_2$ clusters that are based around a general wing-tip butterfly core, and that behave as
25 Single-Molecule Magnets (SMMs).[3b,c] Within this structure the tetra-anionic lower-rim of the calixarene is occupied by one Mn^{III} ion. This moiety can subsequently be exploited in the synthesis of $Mn^{III}_4Ln^{III}_4$ clusters by simple addition of Ln^{III} ions to the reaction mixture used in the formation of the aforementioned
30 $Mn^{III}_2Mn^{II}_2$ SMMs.[3f,g] Depending on the Ln employed in these 3d-4f systems, the resulting materials behave either as a molecular refrigerant (where Ln = Gd) or SMMs (where Ln = Dy or Tb). We also extended our 3d-4f studies to include Fe-Ln mixtures, the result of which was a series of $Fe^{III}_2Ln^{III}_2$ clusters
35 that are markedly different to the $Mn^{III}_4Ln^{III}_4$ motif.[3h] The TBC[4] lower-rim is occupied by one Fe^{III} centre, as has also recently been observed by Redshaw and co-workers in their investigations into calixarene-supported Fe^{III} complexes as procatalysts for ε-caprolactone polymerisation.[4e]

40 Although we recently used TBC[4] as a support in the formation of a small library of clusters, we had not investigated the possibility of forming polynuclear lanthanide clusters with this ligand. The recent re-ignition of interest in the synthesis of polymetallic 4f clusters[5] originates from two major sources:
45 single-molecule magnetism[6] and molecular cooling[7] in which the large magnetic moments, weak exchange and (an)isotropy can be exploited as desired. Here we report the formation of a series of calix[4]arene-supported Ln^{III}_6 clusters, synthesised under facile bench top conditions. Single crystal X-ray structure analysis

50 shows that the metals are arranged at the vertices of an octahedron, with the complexes forming an inter-digitated layer motif which differs markedly to those known for the solvates of TBC[4],[8] and the layered structures formed with the TBC[4]-supported clusters described above.[3] This also represents the first
55 polynuclear lanthanide cluster to be formed with TBC[4], and an important entry into this new system. The reaction of $LnCl_3 \cdot 6H_2O$ and TBC[4] in a basic DMF / ROH (R = Me, Et) solution produces colourless crystals of $[Ln_6(TBC[4])_2O_2(OH)_{3.32}Cl_{0.68}(HCO_2)_2(DMF)_8(H_2O)_{0.5}]$ (**1** = Gd;
60 **2** = Tb; **3** = Dy; **4** = Ho; Figure 1) after slow evaporation of the mother liquor.[‡]
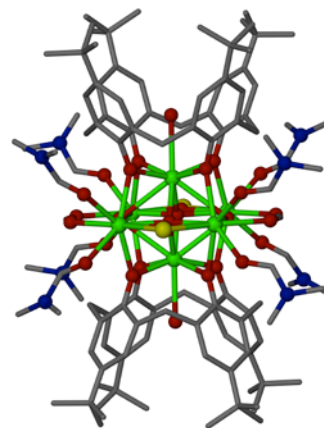
Figure 1. Single crystal X-ray structure of compound **2**. Additional solvent molecules and hydrogen atoms are omitted for clarity. Colour
65 code: Ln = green, O = red, N = dark blue, C = grey, Cl = yellow. The complex is shown in one of two disordered positions.

Crystals of **1** – **4** are in the monoclinic space group $C2/m$ and all are found to be isostructural. Problems with poor diffraction hampered full structure solutions for compounds **1**, **3** and **4**, but
70 full analysis was possible with synchrotron diffraction data collected for **2**. As the four TBC[4]-supported clusters are structurally analogous we provide a generic description. In each case the structures are disordered over two closely related positions, with additional disorder in some ligands (see CIF file
75 for details), and thus we avoid giving detailed bond lengths and angles (although major connectivities are describable). The metallic core (Figure 2) describes a $[Ln^{III}_6]$ octahedron [Ln1...Ln2,3 ~3.4 Å; Ln2...Ln3, ~4.4 Å; Ln1...Ln1', ~3.4 Å] in which the six metal ions are connected internally by two μ_4-O_2^-
80 ions (O1 and symmetry equivalent, s.e; Ln...O, ~2.2 Å). The fully deprotonated TBC[4] ligands house the apical Ln ions (Ln1

and s.e.; Ln…O, ~2.3 Å) within their lower-rim polyphenolic pockets, with each of the four O-arms further bridging to a Ln ion (Ln2, Ln3 and s.e.) in the central metal square. The edges of this square are bridged by a disordered combination of formate (formed *via* the in-situ oxidation of the MeOH solvent) / OH⁻ (O2), and Cl⁻/OH⁻ (O3). The remaining coordination sites on the metal ions are filled with terminally bonded DMF molecules. The apical Ln ions are either of nine-coordinate tri-capped trigonal prismatic geometry when partial occupancy apical aquo ligands are present, or square anti-prismatic geometry in their absence, as shown in Figure 2. The peripheral Ln ions are all of eight-coordinate distorted square anti-prismatic geometry with disorder evident between the chloride an hydroxide ligands as shown in Figure 2.
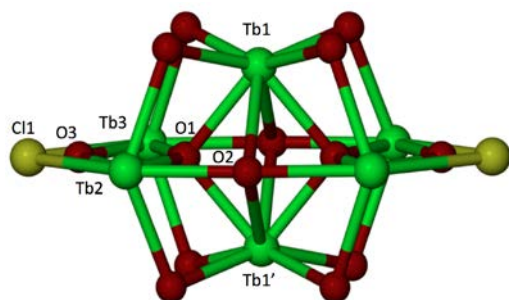


Figure 2. The magnetic core in the structure of **2**.

In our previous studies we have found that TBC[4]-supported clusters (e.g. $Mn^{III}_2Mn^{II}_2$ SMMs) typically adopt the normal packing behaviour of the free ligand,[3] *i.e.* the formation of bi-layers in which the upper-rim tert-butyl groups are arranged in either head-to-head capsule or offset arrangements. Examination of the extended structure in **2** shows that neighbouring complexes pack in an inter-digitated layer structure in which upper-rim tert-butyl groups are sandwiched between the aromatic regions of TBC[4]s from adjacent layers (Figure 3). We postulate that this may be due to the increased coordination number of the peripheral metals in the cluster core relative to the $Mn^{III}_2Mn^{II}_2$ SMMs, for example.[3b,c] This, in addition to the concomitantly increased periphery bulk due to the DMF ligands, may cause steric issues that subsequently force the inter-digitation motif shown in Figure 3, although this will be the topic of future study.

Dc magnetic susceptibility measurements on a powdered crystalline sample of **1** were performed in the 300-2 K temperature range in an applied field of 0.1 T and are plotted as the $\chi_M T$ product versus T in Figure 4. The high temperature value of 46.7 cm³ K mol⁻¹ is near that expected for a spin-only [Gd^{III}_6] moiety (47.25 cm³ K mol⁻¹). The $\chi_M T$ product remains essentially constant as the temperature is decreased, until approximately T = 75 K where it begins to drop rapidly to a value of ~22.5 at 2 K. This behaviour is clearly indicative of very weak antiferromagnetic exchange. The susceptibility data for complex **1** can be successfully simulated employing a 1*J*-model ($\mathcal{H}$ = -$2J\hat{S}_i \cdot \hat{S}_j$)) which assumes all the Gd…Gd interactions are equivalent. Although structurally this is not the case, the crystallographic disorder dictates we employ the simplest of models. The simulation (solid red line in Figure 4) affords J = -0.046 cm⁻¹ with g fixed at 2.00. The magnetisation (M) versus field data for T = 10 K, 4 K and 2 K and B_o ≤ 7 T) are also

reasonably well produced with this simple model (see inset of Figure 4). The magnetic behaviour of complexes **2**-**4** did not show any signs of slow magnetic relaxation; an interesting observation given the enormous thermal energy barrier for the relaxation of the magnetisation (528 K) measured for the structurally similar (square-based pyramidal) complex [$Dy_5O(OtBu)_{13}$].[9]
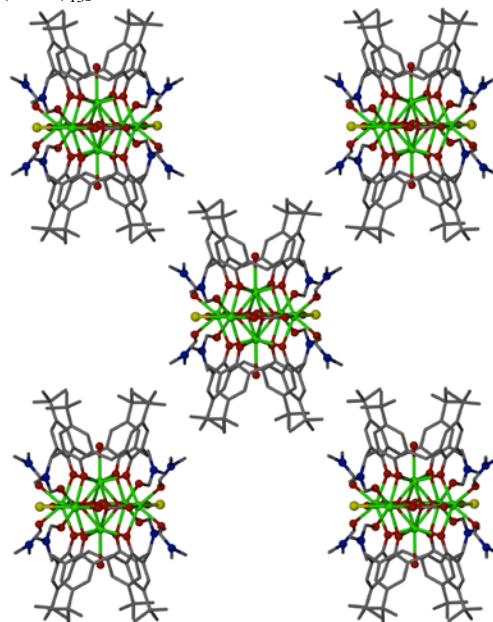
Figure 3. Extended structure of **2** showing the interdigitated layer assembly of TBC[4] with tert-butyl groups of the central complex arranged within adjacent layers. Hydrogen atoms and additional co-crystallised MeCN and DMF molecules (occupying TBC[4] cavity space and interstitial sites between neighbouring complexes respectively) are omitted for clarity.
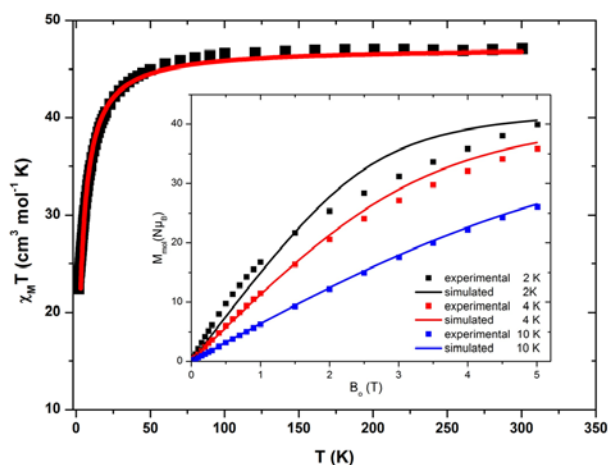
Figure 4. Plot of $\chi_M T$ versus T for complex **1** in an applied field of 0.1 T. The solid red line is a simulation of the experimental data ($\mathcal{H}$ = -$2J\hat{S}_i \cdot \hat{S}_j$)) which assumes all the Gd…Gd interactions are equivalent, affording J = -0.046 cm⁻¹ with g = 2.00. Inset: plot of magnetisation versus field in the indicated ranges; the solid line is a simulation employing the parameters above.

To conclude we have reported the facile synthesis of a series of calix[4]arene-supported Ln^{III}_6 clusters which represent an entry

into polynuclear lanthanide assemblies with this ligand. Given the versatility of the calix[*n*]arenes, a large number of magnetically interesting TM, Ln and 3d-4f assemblies may potentially be formed.[9] In our previous studies we showed that addition of lanthanides to the reaction mixture used to form the $Mn^{III}_2Mn^{II}_2$ SMMs resulted in the formation of new clusters that behaved as molecular refrigerators or SMMs depending on secondary metal employed.[3f,g] This development showed that a common Mn^{III}-calix[4]arene moiety was prevalent in structure formation. It may also therefore be the case that, with careful control over reaction conditions, isolation of a Ln^{III}-calix[4]arene analogue will allow for the construction assemblies of diverse stoichiometry, as well as other new cluster motifs that will be of interest from both a structural and magnetic point of view. These studies are currently underway with a view to monitoring a) the dominant factors in metal ion sequestration by the TBC[4] lower-rim, b) the resulting effect on cluster formation in 3d-4f systems and c) the effect of ligated solvent species on bi-layer formation in the solid state with a view to expressing control over self-assembly.

Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic Information File for **2** (CIF). See DOI: 10.1039/b000000x/

‡ **Synthesis of 1 – 4:** In a general procedure, $LnCl_3 \cdot 6H_2O$ (1 mmol) and TBC[4] (324 mg, 0.5 mmol) were dissolved in a mixture of DMF (10 ml) and ROH (R = Me or Et, 10 ml). After 5 minutes of stirring, NEt_3 (1.2 ml, 9 mmol) was added and the solution stirred for a further 2 h. Colourless block-like crystals were obtained in all cases in excellent yields after filtration (to remove any remaining undissolved material) and diffusion of CH_3CN into the mother liquor. Compound **1**: Yield 87%. Elemental analysis (%) calculated (found) for $C_{120}H_{177.82}Gd_6N_{10.5}O_{26.82}Cl_{0.68}$ (3164.30): C 45.55 (45.88), H 5.66 (5.94), N 4.65 (4.86). Compound **2**: Yield 83%. Elemental analysis (%) calculated (found) for $C_{120}H_{177.82}Tb_6N_{10.5}O_{26.82}Cl_{0.68}$ (3174.35): C 45.40 ( ), H 5.65 (5.91), N 4.63 (4.90).Compound **3**: Yield 79%. Elemental analysis (%) calculated (found) for $C_{120}H_{177.82}Dy_6N_{10.5}O_{26.82}Cl_{0.68}$ (3195.80): C 45.10 (45.21), H 5.61 (5.77), N 4.60 (4.74). Compound **4**: Yield 86%. Elemental analysis (%) calculated (found) for $C_{120}H_{177.82}Ho_6N_{10.5}O_{26.82}Cl_{0.68}$ (3210.38): C 45.89 (46.20), H 5.58 (5.68), N 4.58 (4.29). **General crystallographic details:** Unit cell parameters for compounds **1** and **3** were determined on a Bruker Apex II CCD Diffractometer operating at 100(2) K with MoKα radiation (λ = 0.7107 Å). Data for compound **2** was collected on a Bruker Apex II CCD Diffractometer at 100(2) K with synchrotron radiation (λ = 0.77490 Å). Comparison of unit cell parameters for **1** and **3** with those of the fully resolved structure of **2** identify that **1 – 3** are isostructural. **Unit cell parameters for 1:** Colourless Block, monoclinic, space group *C*2/*m*, *a* = 23.0463(28), *b* = 27.6415(32), *c* = 15.0835(26) Å, β = 129.005(11), *V* = 7305.15 Å³. **Crystal data for 2:** $C_{120}H_{177.82}Cl_{0.68}N_{10.50}O_{26.82}Tb_6$, *M* = 3174.29, Colourless Block, 0.60 × 0.14 × 0.08 mm³, monoclinic, space group *C*2/*m*, *a* = 23.0676(7), *b* = 27.8648(8), *c* = 15.1771(5) Å, β = 129.074(2), *V* = 7573.5(4) Å³, *Z* = 2, $2\theta_{max}$ = 73.5°, 130205 reflections collected, 14527 unique (R_{int} = 0.0543). Final *GooF* = 1.070, *R1* = 0.0484, *wR2* = 0.1622, *R* indices based on 10969 reflections with I

>2sigma(I) (refinement on F^2). **Unit cell parameters for 3:** Colourless Block, monoclinic, space group *C*2/*m*, *a* = 23.1861(31), *b* = 27.7784(34), *c* = 15.1705(7) Å, β = 129.122(4), *V* = 7580.31 Å³. **Unit cell parameters for 4:** Colourless Block, monoclinic, space group *C*2/*m*, *a* = 22.8734(34), *b* = 27.3633(38), *c* = 15.0056(21) Å, β = 128.939(15), *V* = 7305.15 Å³.

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