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Calixarene-supported rare-earth clusters: Heteroatom bridge controls cluster composition**

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Abstract

Rare-earth octahedra have been previously synthesised using *p*-tert-butylcalix[4]arene as a cluster support. Introduction of a heteroatom bridge in the calixarene framework, with concomitant alteration to the nature of the metal binding pocket, results in control over the lanthanide composition in the cluster.

Introduction

Methylene-bridged calix[4]arenes have recently emerged as versatile bowl-shaped ligands for novel polynuclear metal cluster formation. We (amongst others) have shown that the lower-rim polyphenolic character can be used to bind either transition or lanthanide metal centres (TM and LnM respectively) at the centre of the lower-rim as shown in Figure 1A.¹ Using *p*-tert-butylcalix[4]arene or calix[4]arene (TBC[4] and C[4] respectively), we assembled and reported the formation of a) $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ Single-Molecule Magnets (SMMs, Fig. 1B),^{1b,c} b) $[\text{Cu}^{\text{II}}_9(\text{TBC}[4])_3]$ clusters^{1d} that are versatile anion binding materials (Fig. 1C), c) $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ clusters that are magnetic refrigerants or SMMs depending on the lanthanide employed (Fig. 1D),^{1f,g} $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{TBC}[4])_2]$ clusters^{1h} and e) octahedral $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])_2]$ clusters (Fig. 1E).¹ⁱ The thia-, sulfonyl- and sulfinyl-bridged analogues of TBC[4] (Fig. 1F) have received significant attention in the area of cluster formation.² The presence of additional donor atoms markedly affects cluster formation due to necessary ‘migration’ of metals from the centre of the lower-rim basal plane (Fig. 1F).

In contrast to the above oxacalixarenes have received limited attention with respect to TM and LnM cluster formation.³⁻⁶ This is surprising given the fact that controlled introduction of these heteroatom bridges has subtle (yet important) effects on the size of the polyphenolic pocket,⁶ a feature we predicted would have great influence over cluster formation. When comparing TBC[4] to dihomooxacalix[4]arene (Fig. 1G), one can observe a rough geometrical change in the binding pocket moving from square to trapezoidal. *p*-tert-Butyldihomooxacalix[4]arene (TBHOC[4]) has previously been shown to form a $[\text{Eu}^{\text{III}}_2\text{TBHOC}[4])_2]$ assembly with the metal occupying the larger binding site. Given this, in addition to the fact that we were previously able to form $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])]$ clusters under ambient conditions with TBC[4],¹ⁱ we explored the formation of polynuclear LnM clusters with TBHOC[4]. Here we show that reactions similar to those used to form $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])_2]$ clusters afford new $[\text{Ln}^{\text{III}}_5(\text{TBHOC}[4])]$ systems with the calixarene acting as a support ligand.

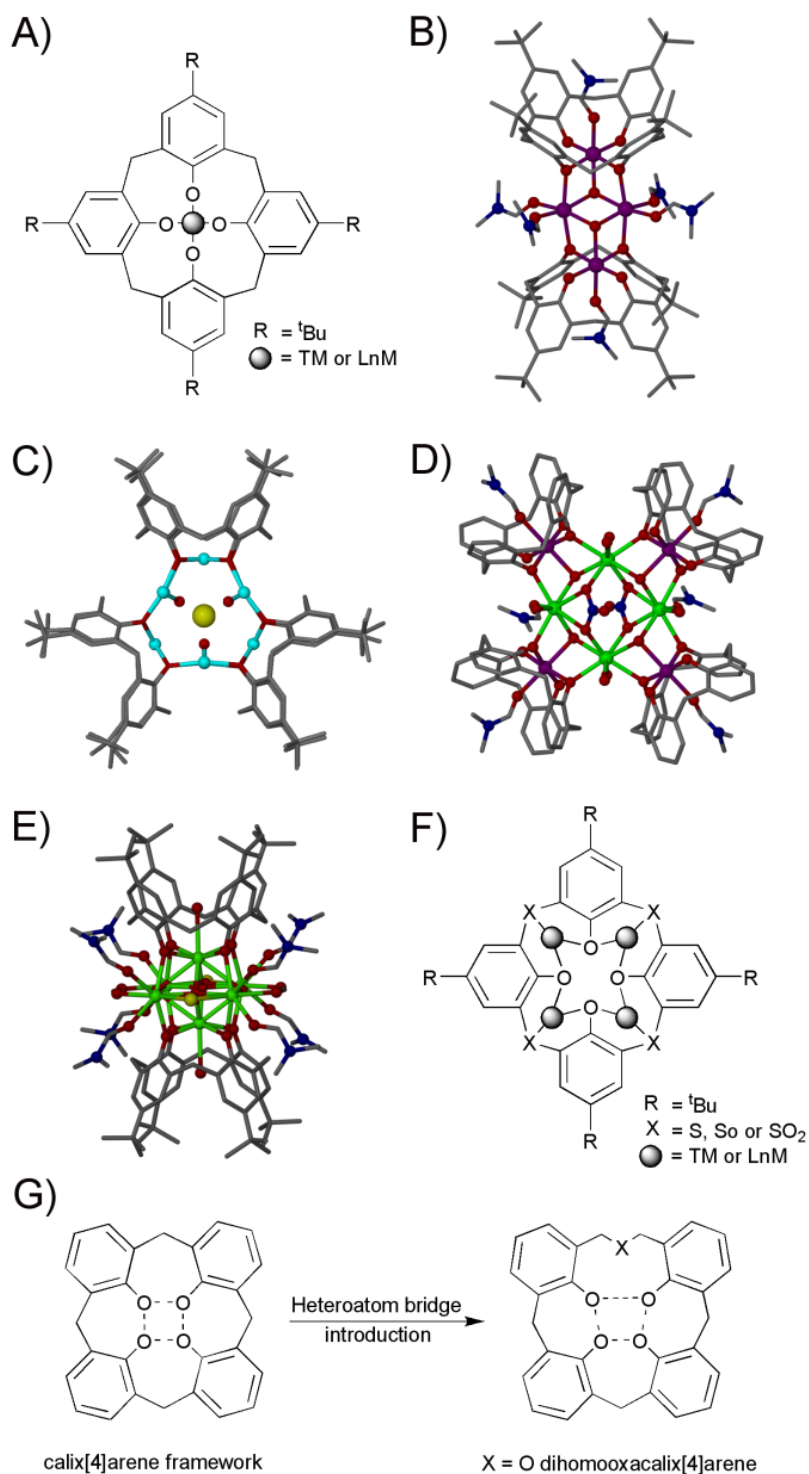


Figure 1. A) General schematic for TM and LnM binding in the C[4] lower-rim polyphenolic pocket. B) [Mn^{III}₂Mn^{II}₂(TBC[4])₂] SMM. C) Tri-capped trigonal prismatic [Cu^{II}₉(TBC[4])₃] cluster with chloride counter ions shown. D) [Mn^{III}₄Ln^{III}₄(C[4])₄] clusters. E) Octahedral [Ln^{III}₆(TBC[4])₂] clusters. F) Alternative TM and LnM binding observed with thia-, sulfonyl- and sulfanyl-C[4]s. G) Change in lower-rim binding site geometry induced by heteroatom bridge introduction. Colour code: Mn – purple, Cu – pale blue, Ln – green, Cl – yellow, O – red, N – blue, C – grey. H atoms omitted for clarity and figures not to scale.

The reaction of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and TBHOC[4] in a basic DMF / MeOH solution, followed by vapour diffusion with Et_2O , produced colourless single crystals of **1** – **3** with general formula $[\text{Ln}^{\text{III}}_5(\text{TBHOC}[4])_2(\text{NO}_3)_3(\mu\text{-MeO})(\mu_4\text{-O})(\mu_3\text{-OH})(\text{dmf})_7(\text{H}_2\text{O})] \cdot (\text{Et}_3\text{NH} \cdot \text{OH}) \cdot (\text{dmf}) \cdot (\text{Et}_2\text{O})_2$ (**1** = Gd; **2** = Tb; **3** = Dy; Fig. 2).[‡] Crystals of **1** are in a monoclinic cell and structure solution was performed in the space group $P2_1/n$. The three calixarene-supported clusters are isostructural and we thus provide a generic description of **1**. The asymmetric unit contains the entire formula of **1**, and structure analysis reveals the Ln^{III}_5 cluster housed within two TBHOC[4]s as shown in Figure 2.

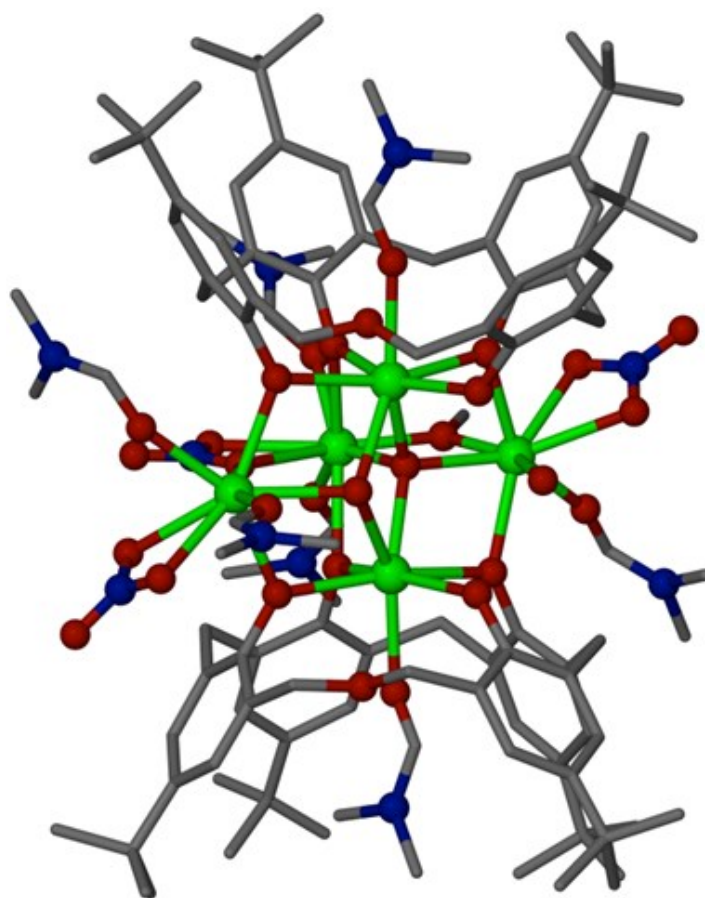


Figure 2. Part of the asymmetric unit in **1** showing the assembly $[\text{Ln}^{\text{III}}_5(\text{TBHOC}[4])_2(\text{NO}_3)_3(\text{dmf})_7(\mu\text{-MeO})(\mu_4\text{-O})(\mu_3\text{-OH})\text{H}_2\text{O}]$. The co-crystallised triethylammonium cation, water molecule and H atoms are omitted for clarity. Disordered TBHOC[4] ^tBu groups are shown in one of two positions.

The metallic core (Fig. 3A) describes a distorted $[\text{Ln}^{\text{III}}_5]$ square pyramid, the base of which is near-planar [Gd1...Gd5, 3.730 Å; Gd5...Gd2, 3.731 Å; Gd2...Gd3, 3.838 Å; Gd3...Gd1, 3.860 Å;], while the pyramidal vertex is skewed to one side, resulting in one long Gd...Gd distance [Gd1...Gd4, 3.730 Å; Gd5...Gd4, 3.623 Å; Gd2...Gd4, 3.715 Å; Gd3...Gd4, 4.784 Å]. The five metal ions are

connected by one $\mu_4\text{-O}^{2-}$, one $\mu_3\text{-OH}^-$, one $\mu\text{-MeO}^-$, and along the longest Gd...Gd connectivity, a bridging and chelating nitrate anion as shown in Figure 3. The fully deprotonated TBHOC[4]s house the Gd1 and Gd2 ions within their lower-rim polyphenolic pockets, and three of the four O-atoms further bridge to Gd ions (Gd3, Gd4 or Gd5, Fig. 3A). This overall arrangement is thus markedly different to that observed in the $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])_2]$ cluster,¹¹ albeit with inclusion of bridging nitrate anions rather than chlorides. The remaining coordination sites on the metal ions are filled with seven terminally bonded DMF molecules, one ligated water and two chelating nitrate anions (Fig. 2). The two calixarene-bound Gd ions (Gd1 and Gd2) reside slightly out of the plane of the lower-rim O-atoms and both are seven coordinate and distorted pentagonal bipyramidal in geometry. The remaining three Gd ions are all eight coordinate and square antiprismatic, as shown in Figure 2.

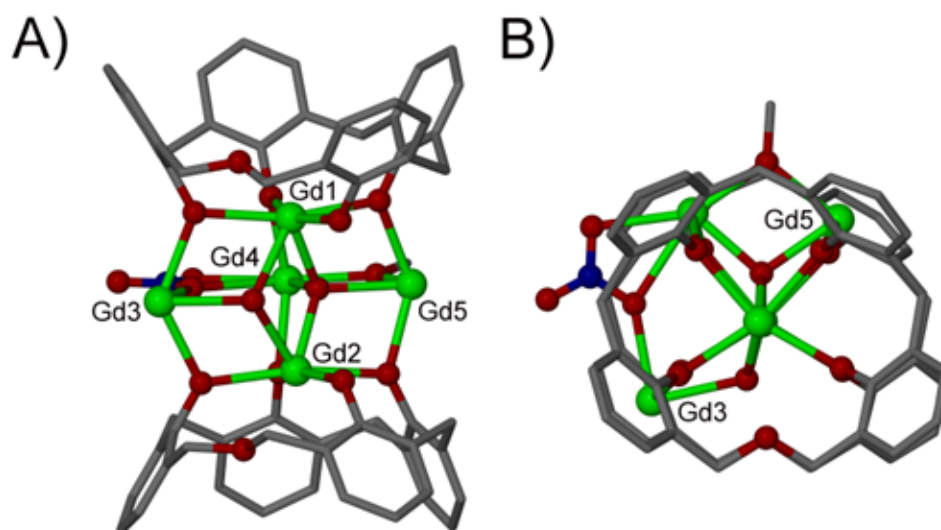
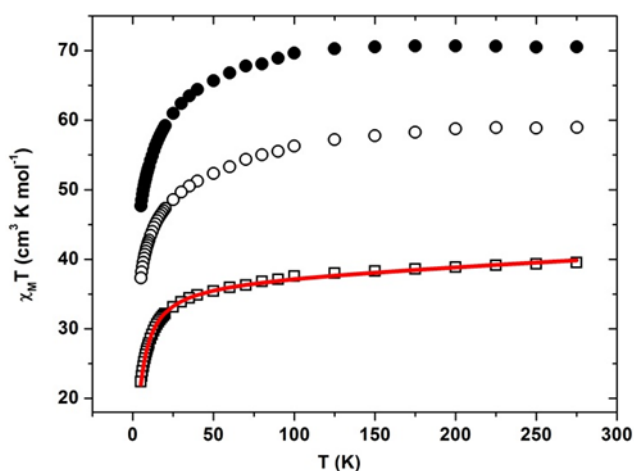


Figure 3. A) Partial structure of **1** showing the magnetic core. B) Orthogonal view showing the eclipsed nature of the calixarene heteroatom bridges.

Further examination of the cluster suggests that a small binding pocket, presented by the $\mu_4\text{-O}^{2-}$, $\mu_3\text{-O}^-$, the two terminal TBHOC[4] lower-rim O-atoms and the ligated water of Gd5, may allow us to introduce an additional TM centre, either during or post-synthesis, a feature we are currently exploring. Indeed this pocket is currently filled with a $\text{Et}_3\text{NH}\cdot\text{OH}$ cation-anion pair with the O-atom of the hydroxide H-bonded or in close contact with all of the aforementioned O-atoms (O...O, 2.693-3.281 Å). There are also intramolecular H-bonds between adjacent nitrate O-atoms (O...O, 2.793 Å), phenolic O-atoms and the terminally bonded H_2O (O...O, ~2.68 Å) and the phenolic and heteroatom O-atoms (O...O, ~3.0 Å). Examination of the extended structure shows that the clusters pack in a manner akin to the bi-layer assembly observed for $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])_2]$.



← **Figure 4.** Plot of $\chi_M T$ versus T for complexes **1** (\square), **2** (\circ) and **3** (\bullet) in an applied field of 0.1 T and the 275 – 5 K temperature range. The solid red line is a fit of the experimental data; see text for details.

The dc magnetic susceptibility data for complexes **1-3** is plotted in Figure 4 in the form of $\chi_M T$ versus T . In each case the high temperature values ($39.5 \text{ cm}^3 \text{ K mol}^{-1}$ (**1**); $59.0 \text{ cm}^3 \text{ K mol}^{-1}$ (**2**) and $70.6 \text{ cm}^3 \text{ K mol}^{-1}$ (**3**)) are those expected for five non-interacting Gd^{3+} ($4f^7$, $^8S_{7/2}$, $g=2$), Tb^{3+} ($4f^8$, 7F_6 , $g=3/2$) and Dy^{3+} ($4f^9$, $^6H_{15/2}$, $g=4/3$) ions, respectively. As temperature is decreased the value of $\chi_M T$ drops only very slowly to approximately 25 K, where the decline is a little steeper. This behaviour is clearly indicative of very weak intra-molecular antiferromagnetic exchange, as would be expected for alkoxide-bridged 4f ions. The susceptibility data for complex **1** can be successfully fitted employing an isotropic $1J$ -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, this simple model works well, the fit (solid red line in Figure 4) affording $J = -0.060 \text{ cm}^{-1}$ with g fixed at 2.00. This, perhaps unsurprisingly, is very close to the value ($J = -0.046 \text{ cm}^{-1}$) obtained for the structurally similar TBC[4]-based $[\text{Gd}_6]$ octahedron.¹¹

The magnetic behaviour of complexes **2-3** did not show any signs of slow magnetic relaxation, i.e. no out-of-phase (χ_M'') signals in ac susceptibility nor hysteresis loops in dc magnetisation versus field scans; an interesting observation given the enormous thermal energy barrier for the relaxation of the magnetisation observed in a structurally similar alkoxide-bridged $[\text{Dy}_5]$ square pyramid.^{7,8}

Conclusions

We have shown that the introduction of a heteroatom bridge to the calix[4]arene framework permits facile control over the number of LnMs included in C[4]-supported cluster formation. It is possible to introduce > 1 heteroatom bridge of this type by convergent synthesis, and we predict that this will allow us to further tune both the metal composition of the resulting structures. This work is currently underway with a view to obtaining said control over both structure and thus magnetic properties. In addition we are also exploring the possibility of additional TM inclusion in the aforementioned binding pocket, either during or post-synthesis. This work is underway and will be reported in due course.

Notes and references

‡TBHOC[4] was prepared according to literature procedure.^Z **Synthesis of 1:** Gd(NO₃)₃.6H₂O (131 mg, 0.3 mmol) and TBHOC[4] (100 mg, 0.15 mmol) were dissolved in a 1:1 v/v mixture of MeOH/dmf (12 ml). After 10 min of stirring, Et₃N (0.1 ml) was added and the solution stirred for a further hour. During this period a precipitate formed and this was removed by filtration to leave a colourless solution. Colourless crystals of **1** were obtained by vapour diffusion with Et₂O. Elemental analysis (%) calculated for **1**, C₁₁₂H₁₆₀O₃₀N₁₀Gd₅: C, 46.18 %; H, 5.54 %; N, 4.81 %. Found: C, 45.79 %; H, 6.03 %; N, 5.24 %. **Synthesis of 2 and 3:** These were synthesised in an analogous manner using Tb(NO₃)₃.xH₂O and Dy(NO₃)₃.5H₂O, respectively, in place of Gd(NO₃)₃.6H₂O. Elemental analysis (%) calculated for **2**, C₁₁₂H₁₆₀O₃₀N₁₀Tb₅: C, 46.05 %; H, 5.52 %; N, 4.79 %. Found: C, 45.30 %; H, 5.87 %; N, 4.71 %. Elemental analysis (%) calculated for **3**, C₁₁₂H₁₆₀O₃₀N₁₀Dy₅: C, 45.77 %; H, 5.49 %; N, 4.77 %. Found: C, 45.44 %; H, 5.90 %; N, 4.68 %.

General crystallographic details: Data were collected on a Bruker Apex II diffractometer operating at 100(2) K with Mo-K α radiation (0.71073 Å). Full structural analysis was carried out for **1**, while unit cell parameters were used to confirm the isostructural nature of **2** and **3**. The routine SQUEEZE was applied to the data in refinement of **1** due to disorder associated with co-crystallised Et₂O and dmf molecules that could not be modelled appropriately. This had the effect of markedly improving the

Crystal data for 1: C₁₁₂H₁₆₀O₃₀N₁₀Gd₅, $M = 2913.07$, colourless needle, space group $P21/n$, $a = 21.813$, $b = 29.655$, and $c = 24.765$ Å, $\alpha = 90.0$, $\beta = 118.316$, and $\gamma = 90.0^\circ$, $V = 14102.79$ Å³, $Z = 6$, $D_c = 1.741$ g/cm³

Unit cell parameters for 2: $a = 21.7205(12)$, $b = 29.7210(14)$, and $c = 23.9371(13)$ Å, $\beta = 114.631(2)$, $V = 14046.68$ Å³.

Unit cell parameters for 3: $a = 21.921(?)$, $b = 30.123(?)$, and $c = 24.172(?)$ Å, $\beta = 114.333(?)$, $V = 14046.68(?)$ Å³.

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