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## Exploratory studies into 3d/4f cluster formation with fully bridge-substituted calix[4]arenes

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*Dedicated to Professor Jerry L. Atwood on the occasion of his 75<sup>th</sup> birthday.*

Supporting information (additional figures to support discussion and crystallographic

information files, CIFs) can be accessed at <https://doi.org/.....>

# Exploratory studies into 3d/4f cluster formation with fully bridge-substituted calix[4]arenes

Calix[4]arenes are extremely versatile ligands that are capable of supporting the formation of a wide variety of polymetallic clusters of paramagnetic metal ions. One can exert influence over cluster formation through alteration of the calix[4]arene framework and subsequent ‘expansion’ of the lower-rim polyphenolic binding site. The present contribution investigates cluster formation with calix[4]arenes substituted at all four methylene bridge positions with furan moieties. Two known cluster types have been isolated with this ligand, the structures of which lend insight into factors that may ultimately preclude the formation of mixed-metal species.

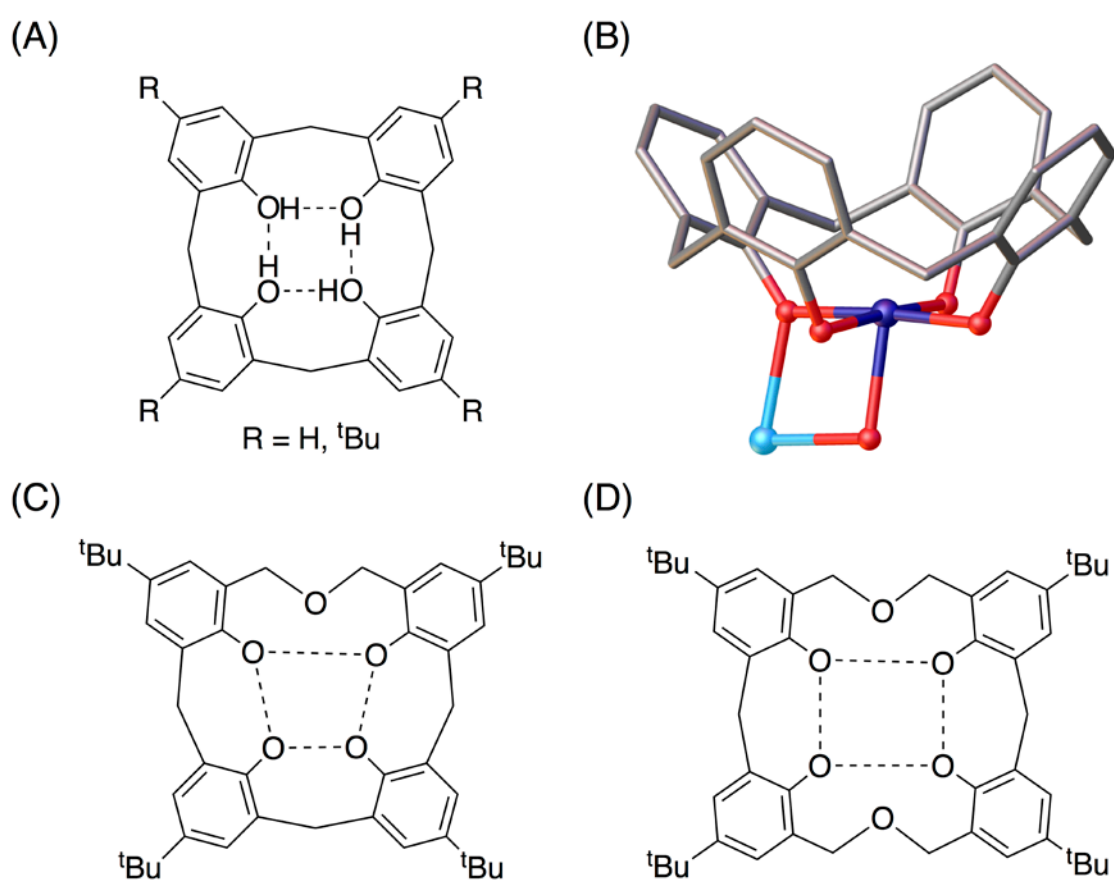
**Keywords:** Calixarenes; Coordination Chemistry; Clusters; Synthesis; Crystallography

*Dedicated to Professor Jerry L. Atwood on the occasion of his 75<sup>th</sup> birthday.*

## 1. Introduction

The ability to influence the formation of paramagnetic metal ion clusters from multi-component systems is a challenging synthetic goal that holds great potential when considering the possibility to control or fine tune physical properties such as molecular magnetism (1-5). We have found that methylene-bridged calix[4]arenes (cyclic tetraphenols, collectively termed C[4]s hereafter, Figure 1A), are remarkably versatile ligands for cluster synthesis under ambient conditions, affording a wide range of structural topologies as a result (6-12). This is primarily due to their possessing a tetraphenolic pocket that readily binds 3d or 4f metal ions when deprotonated with a suitable base. These phenolato groups bridge to neighbouring ions within a cluster (for example see Figure 1B) and impart a degree of directionality in the assembly process; this can also be considered as structural capping behaviour (*vide infra*). C[4]-supported clusters can also be synthesised under solvothermal (13,14) or air-sensitive conditions

(15-17), but discussion of this expansive chemistry is far beyond the scope of this contribution; in these cases the resulting structures differ markedly from those reported herein. Thia-, sulfonyl- and sulfinyl-bridged C[4]s have also been used in cluster-forming chemistry, but lower-rim coordination chemistry is drastically different to that of the methylene-bridged analogues, leading to vastly different structure types and physical properties. Again, this is far outwith the scope of this manuscript, but the reader is directed to recent reviews on the subject (18-20).



**Figure 1.** A) Schematic of calix[4]arene (R = H) and *p*-<sup>t</sup>Bu-calix[4]arene (R = <sup>t</sup>Bu), collectively termed C[4]s. Concerted hydrogen bonding interactions at the tetraphenolic lower-rim are shown as dashed lines between OH groups. B) Section of the single crystal X-ray structure of a C[4]-supported {Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>(OH)<sub>2</sub>} cluster showing wing-tip Mn<sup>III</sup> binding in the tetraphenolato pocket, as well as phenolato and hydroxide bridging to a body Mn<sup>II</sup> ion (7, 11). C) Schematic of dihomooxalix[4]arene showing the distortion to the lower-rim tetraphenolato binding pocket through introduction of

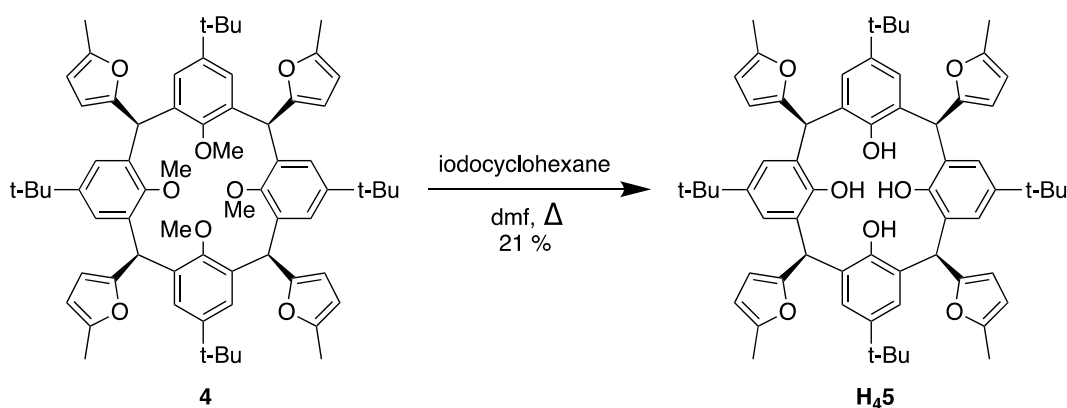
one ethereal bridge, the result of which is a trapezoidal binding pocket. D) Schematic of tetrahomodioxacalix[4]arene showing a rectangular binding pocket that results from 'expansion' through the introduction of distal ethereal bridges. Color code: C – grey, O – red, Mn<sup>III</sup> – dark blue, Mn<sup>II</sup> – pale blue. H atoms omitted in (B) for clarity.

With respect to methylene-bridged C[4]s, the first result of our exploratory investigations into C[4]-supported cluster formation was a series of [Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>(C[4])<sub>2</sub>] SMMs (**1**) that possess a common structural butterfly-like {Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>( $\mu_3$ -OH)<sub>2</sub>} core, half of which is shown in Figure 1B (7, 11). The oxidation state distribution is rare (21), is the reverse of that found in the majority of structural analogues in the literature (22-23), and is driven by the C[4] tetraphenolic pocket which preferentially binds the wing-tip manganese ions in the 3+ oxidation state. The C[4]s bridge to the body ions (in the 2+ oxidation state) and [Mn<sup>III</sup>(C[4])] moieties in the structure can be considered as capping units; these structure capping moieties, the nature of which depends on the metal ions present, are found in every C[4]-supported cluster we have reported to date. With the content of this contribution in mind, a second cluster that is worthy of mention is a [Ln<sup>III</sup><sub>6</sub>( $\mu_3$ -O)<sub>2</sub>( $\mu$ -OH)<sub>3.32</sub>( $\mu$ -Cl)<sub>0.68</sub>(HCOO)<sub>2</sub>(C[4])<sub>2</sub>] species (**2**) in which the lanthanide ions are arranged at the vertices of an octahedron (12). In this case a Ln<sup>III</sup> ion is bound by the tetra-phenolic pocket upon deprotonation, sitting just outside the basal plane of the oxygen atoms, affording a [Ln<sup>III</sup>(C[4])] structural capping moiety as a result. Liao and co-workers reported the solvothermal synthesis of a cluster of formula [Ln<sup>III</sup><sub>6</sub>( $\mu_4$ -O)<sub>2</sub>( $\mu$ -CH<sub>3</sub>O)<sub>2</sub>( $\mu$ -HCOO)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(C[4])<sub>2</sub>] (**3**) (14), the core of which is similar to that of **2**, showing that this is a versatile cluster topology for C[4]. Reactions containing both 3d and 4f ions give several different heterometallic clusters depending on the stoichiometries and metal salts employed (6, 8, 10, 24), an interesting example of which is the ability to systematically interchange the

body ions in the  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3\text{-OH})_2(\text{C}[4])_2]$  butterfly for  $\text{Ln}^{\text{III}}$ ; this affords either  $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}\text{Mn}^{\text{II}}(\mu_3\text{-OH})_2(\text{C}[4])_2]$  or  $[\text{Mn}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\mu_3\text{-OH})_2(\text{C}[4])_2]$  clusters as a result. Our exploratory cluster-forming studies with C[4]s have provided empirical metal ion binding rules as follows: 1) C[4]s will bind  $\text{Mn}^{\text{III}}$  preferentially over  $\text{TM}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  ions; 2) C[4]s will bind  $\text{Fe}^{\text{III}}$  preferentially over  $\text{TM}^{\text{II}}$  ions; 3) C[4]s will bind  $\text{TM}^{\text{II/III}}$  preferentially over Ln ions; 4) C[4]s will bind  $\text{Ln}^{\text{III}}$  in the absence of TM ions. Every structure isolated to date contains either  $[\text{TM}^{\text{III}}(\text{C}[4])^-]$ ,  $[\text{TM}^{\text{II}}(\text{C}[4])^{2-}]$  or  $[\text{Ln}^{\text{III}}(\text{C}[4])^-]$  capping moieties, and these act to cap polyhedral structures in a consistent manner.

In addition to carrying out such exploratory work with C[4], we have also reported on aspects of binding site alteration and the subsequent effect this has on cluster formation / composition (25-27). Our first effort in this regard was to employ oxacalixarenes to systematically vary the size of the tetraphenolato pocket (26-27). The introduction of one or two ethereal bridges between neighbouring aromatic rings ‘expands’ the C[4] framework, giving trapezoidal (Fig. 1c) or rectangular (Fig. 1d) binding pockets respectively. The use of these oxacalixarenes in cluster formation gave markedly different results, an excellent example of which is the isolation of a  $\text{Ln}_5$  cluster that can be considered an analogue of the aforementioned  $\text{Ln}_6$  species. In this case one of the equatorial ions from the octahedron has been omitted due to the targeted ‘expansion’ of the lower-rim binding pocket; this  $\text{Ln}^{\text{III}}$  ion omission coincides directly with the position of the ethereal bridge. We also recently tethered C[4]s with alkyl chains of varying length through synthetic modification at one methylene bridge position (25). In doing so we found cluster formation with these bis-C[4]s to be challenging, except in cases where the tether was long enough to allow the constituent C[4]s to form previously reported cluster topologies (e.g. **1**).

Here we present initial results from a new investigation that aims to explore the limits of cluster formation with C[4]s substituted at all methylene bridge positions. A search of the literature shows that there are relatively few fully substituted C[4]s that can be readily synthesised with all substituted groups equatorial, but one candidate that represented a viable starting point for this work is 5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra(2-methylfuran-yl)-25,26,27,28-tetramethoxycalix[4]arene (**4**, Scheme 1) (28). Compound **4** is synthesised from C[4] in three steps: lower-rim alkylation to afford the tetra-methoxy derivative, monobromination at all four methylene bridge positions and subsequent reaction with 2-methylfuran in the presence of butylene oxide. This affords a C[4] with all furan groups equatorial as shown in Scheme 1.



**Scheme 1.** Deprotection of the lower-rim of **4** to give 5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra(2-methylfuran-yl)-25,26,27,28-tetrahydroxycalix[4]arene, **H45**.

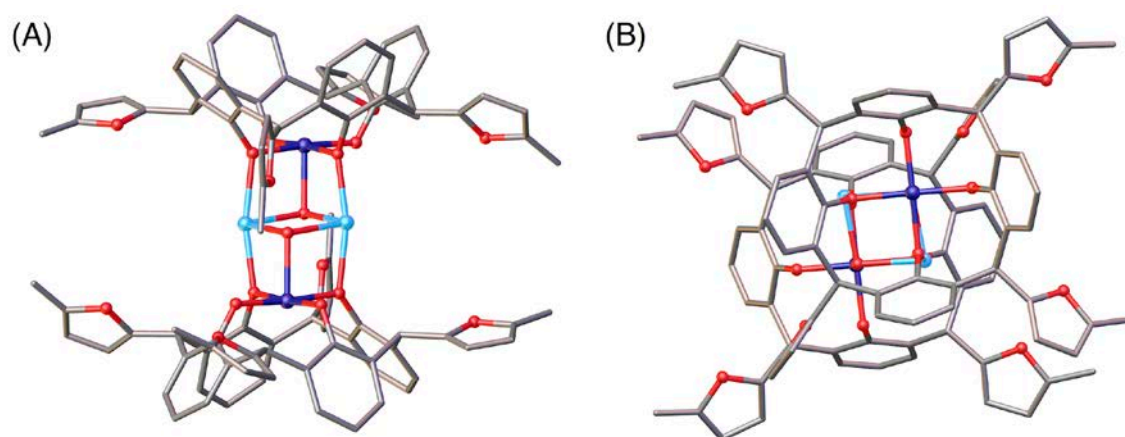
## 2. Results and Discussion

The use of compound **4** in cluster formation (via our typically employed ambient reaction conditions) first required de-protection of lower-rim methoxy groups to afford the required tetraphenolic C[4] pocket for metal ion binding / bridging. This was achieved using iodocyclohexane, giving 5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra(2-methylfuran-yl)-25,26,27,28-tetrahydroxycalix-[4]arene, **H45**, in 21 % yield following purification. Given the frequency with which we have isolated  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3-$

OH)<sub>2</sub>(C[4])<sub>2</sub>] clusters, we selected this as our first target cluster topology. Reaction of **H45** with manganese(II) chloride tetrahydrate in a 1:1 DMF / MeOH mixture (to aid solubility), and in the presence of Et<sub>3</sub>N as a base, rapidly afforded a deep purple solution upon stirring at room temperature. Good quality purple single crystals grew readily following vapour diffusion of petroleum ether into the mother liquor, and subsequent diffraction studies found them to be of formula [Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(**5**)<sub>2</sub>(dmf)<sub>4</sub>(MeOH)<sub>2</sub>](MeOH)<sub>3</sub>(Et<sub>2</sub>O) (**6**). Crystals of **6** were in a triclinic cell and structure solution was carried out in the space group *P*-1. The asymmetric unit (ASU) was found to contain half of the compound formula and, as expected, symmetry expansion revealed formation of the common butterfly cluster topology as shown in Figure 2. Inspection of Figure 2A shows that the furans substituted at the methylene bridge positions are all equatorial as expected, and that they are sufficiently far from the cluster core to prevent interference with solvent ligation at the body Mn<sup>II</sup> ions (ligated solvent is shown in Figure S1); bond lengths and angles relating to the cluster are similar to those of the C[4]-supported analogue, **1** (7, 11). The positioning of the furan groups around the cluster periphery is naturally dictated by the coordination chemistry, and as can be seen in Figure 2B, the two equivalents of **5** are arranged in an offset manner due to the cluster core topology.

With the orientation / positioning of the furan groups in mind, we expanded our investigation to include the formation of 3*d*-4*f* clusters to establish whether: 1) it would be possible to isolate mixed-metal clusters, 2) different stoichiometries would lead to 3*d* / 4*f* metal ion interchange akin to C[4]-supported cluster chemistry, and 3) the furans would play a role in cluster formation, potentially coordinating to Ln<sup>III</sup> ions. We investigated this by exploring three ratios of Mn:Ln (Dy/Tb/Gd) ion present in the reaction mixture, these being 4:1, 1:1 and 1:4.





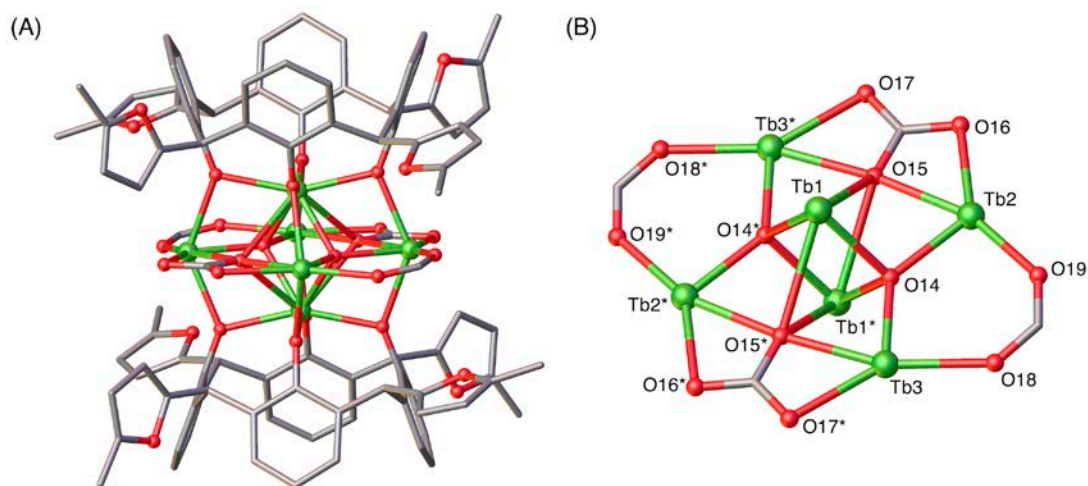
**Figure 2.** Views of the single crystal X-ray structure of **6**. A) Side-on view showing formation of the expected mixed-valence  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3\text{-OH})_2]$  core that is supported by two tetra-anions of **H45**. B) View down the cavity of **5** clearly showing  $\text{Mn}^{\text{III}}$  ion binding in the tetra-phenolato pocket and the orientation of furan groups on the methylene bridge positions. Color code: C – grey, O – red,  $\text{Mn}^{\text{III}}$  – dark blue,  $\text{Mn}^{\text{II}}$  – pale blue. Solvent of crystallisation, H atoms and ligated solvent molecules are omitted for clarity.

The first set of single crystals that were isolated were purple, and these arose from the reaction involving a 1:1 ratio of Mn:Tb ions. The crystals were found to be in a triclinic cell and structure solution was carried out in the space group  $P\bar{1}$ . Somewhat surprisingly, the crystals were found to be of formula  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3\text{-OH})_2(\mathbf{5})_2(\text{dmf})_6][\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3\text{-OH})_2(\mathbf{5})_2(\text{dmf})_{5.5}(\text{H}_2\text{O})_{0.5}](\text{dmf})_2$ , **7**, indicating that  $4f$  ions were not involved in cluster formation; this is atypical for C[4]-supported clusters formed in the presence of such ion mixtures. The ASU was found to contain half of the aforementioned formula, and symmetry expansion afforded two butterflies (Figure S2) that are closely related to the structure of **6**. Upon inspection, one noticeable difference upon moving to **7** is that one of the butterflies possesses six ligated dmf molecules, as opposed to four dmf and two MeOH in **6**. The second butterfly is also different as,

although it also possesses four peripherally ligated dmf molecules, the cavities of symmetry equivalents of **5** are occupied by disordered water (ligated) and dmf (non-ligated). As in the case of **6**, the cluster cores found in **7** are closely related to their respective C[4]-supported cluster analogue (**1**).

The only other set of crystals that were obtained from the current set of experiments were colourless, arising from the reaction involving a 1:4 ratio of Mn:Tb ions. The crystals were in a monoclinic cell, and structure solution in space group  $P2_1/n$  revealed these to be of formula  $[\text{Tb}^{\text{III}}_6(\mu_4\text{-O})_2(\mu\text{-HCOO})_2(\mu_4\text{-CO}_3)_2(\mathbf{5})_2(\text{dmf})_8(\text{H}_2\text{O})_8](\text{MeOH})_2(\text{H}_2\text{O})_2$  (**8**). The asymmetric unit was found to contain half of the aforementioned formula, with symmetry expansion giving rise to the cluster shown in Figure 3. Inspection of the structure shows that this overall cluster topology conforms to the previously reported lanthanide octahedra discussed in the introductory section, but in this case there is yet another variation in the nature of anions in and around the cluster core. Figure 3B shows the central core with tetra-anions of **H45** omitted for clarity. As can be seen, the inner part of the core contains two  $\mu_4$ -oxides that bridge Tb1, its symmetry equivalent (s.e., Tb1\*), Tb2 and Tb3. This is a common feature to all three  $\text{Ln}^{\text{III}}$  octahedra (*12*, *3*), as is the presence of two peripheral bridging formate anions (e.g. see Figure 3B, O18 / O19 and s.e. O18\* / O19\*). The main difference observed upon moving from either **2** or **3** to **8** is the introduction of the  $\mu_4\text{-CO}_3^{2-}$  (O15 / O16 / O17 and O15\* / O16\* / O17\*) anions in place of  $\mu\text{-OH}^- / \mu\text{-Cl}^-$  and  $\mu\text{-CH}_3\text{O}^- / \text{terminal NO}_3^-$  respectively. We propose that the bridging formate and carbonate anions originate from decomposition of dmf; this is commonplace for such reactions involving C[4] as a cluster support. As is the case in **2**, each of the four  $\text{Tb}^{\text{III}}$  ions in the central plane of the cluster possesses two ligated dmf molecules that, together, can be seen to define the vertices of a near-perfect square prim (Figure S3).

These eight ligated dmf molecules are positioned between the furan moieties at the calixarene bridge positions, further indicating that these cluster topologies are capable of withstanding the introduction of relatively large moieties to the supporting ligand framework.



**Figure 3.** Views of the single crystal X-ray structure of **8**. (a) Side-on view showing formation of the  $[\text{Tb}^{\text{III}}_6(\mu_4\text{-O})_2(\mu\text{-HCOO})_2(\mu_4\text{-CO}_3)_2]$  core that is supported by two tetra-anions of **H45**. (b) View of the central core with selected atoms labelled according to discussion. Color code: C – grey, O – red,  $\text{Tb}^{\text{III}}$  – green. Solvent of crystallisation, H atoms and ligated solvent molecules are omitted for clarity.

The magnetic properties of clusters **6** – **8** were not investigated, as all are very closely related to previously published topologies and can be expected to be very similar.

### 3. Conclusions

To conclude, we have shown that a C[4] substituted at all methylene bridge positions can be de-protected at the lower-rim and successfully used in the synthesis of 3d or 4f clusters. The three species isolated conform to two known types reported for analogous C[4]-supported cluster chemistry, and the fact that 3d-4f clusters were not isolable

suggests that the presence of furan moieties at the C[4] bridge positions hinders mixed-metal cluster formation. This may be due to the increased coordination number / presence of additional ligands around the cluster periphery, but further investigation is required in order to confirm this hypothesis. This will be the subject of future work in the area of fully bridge-substituted C[4]-supported cluster chemistry and results will be reported in due course, including magnetic properties of clusters isolated if these are found to deviate from existing topologies.

#### 4. Experimental

Compound **4** was synthesised according to literature procedures and purity was confirmed by  $^1\text{H}$  NMR prior to use (28). **Synthesis of 5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra(2-methylfuran-2-yl)-25,26,27,28-tetrahydrocalix[4]arene, H45:** Cyclohexyl iodide (9.86 g, 46.91 mmol) was added to a stirred suspension of compound **4** (1.069 g, 1.04 mmol) in DMF (60 mL) and the reaction was heated at reflux for 48 hours. The resulting brown solution was cooled to RT before being poured into water (100 mL), leading to the precipitation of a brown solid. This solid was collected by filtration and stirred as a suspension in MeOH for 15 minutes. Subsequent filtration afforded a yellow crude that was recrystallised from  $\text{CHCl}_3/\text{MeOH}$  to yield 0.210 g (21 %) of pure **H45**.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 8.94 (br. s., 4 H) 7.16 (s, 8 H) 6.14 (d,  $J=2.57$  Hz, 4 H) 5.94 (d,  $J=2.90$  Hz, 4 H) 5.90 (s, 4 H) 2.28 (s, 12 H) 1.11 (s, 36 H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 152.75, 151.44, 146.19, 143.80, 128.39, 124.01, 109.74, 105.76, 37.31, 34.18, 31.20, 13.61. MS (MALDI-TOF): 991.5,  $[\text{M}+\text{Na}]^+$ .

**Synthesis of  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\mu_3\text{-OH})_2(\mathbf{5})_2(\text{dmf})_4(\text{MeOH})_2](\text{MeOH})_3(\text{Et}_2\text{O})$ , **6:****  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (40.9 mg, 0.207 mmol) and **H45** (50.0 mg, 0.052 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring  $\text{Et}_3\text{N}$  (0.045 mL) was

added and the resulting deep purple solution was stirred at RT for 2 hours. The reaction mixture was filtered to remove any microcrystalline material, and purple crystals of **6** grew upon vapour diffusion of petroleum ether into the mother liquor. These were found to be sensitive towards solvent loss upon removal of the mother liquor, and sample homogeneity was assessed by multiple unit cell determinations. **Crystal data for 6 (CCDC 1583896):** C<sub>149</sub>H<sub>196</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>28</sub>, *M* = 2710.85 g/mol, triclinic, space group *P*-1 (no. 2), *a* = 13.1012(9) Å, *b* = 17.0409(11) Å, *c* = 17.5344(12) Å, *α* = 72.026(3)°, *β* = 86.362(3)°, *γ* = 87.172(3)°, *V* = 3714.3(4) Å<sup>3</sup>, *Z* = 1, *T* = 100(2) K, MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å), 57869 reflections measured (2.444° ≤ 2 $\Theta$  ≤ 54.174°), 15969 unique (*R*<sub>int</sub> = 0.1222, *R*<sub>sigma</sub> = 0.2345) which were used in all calculations. The final *R*<sub>1</sub> was 0.0864 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.2787 (all data).

**Synthesis of [Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>( $\mu$ <sub>3</sub>-OH)<sub>2</sub>(5)<sub>2</sub>(dmf)<sub>6</sub>][Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>( $\mu$ <sub>3</sub>-OH)<sub>2</sub>(5)<sub>2</sub>(dmf)<sub>5.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>](dmf)<sub>2</sub>, **7:** MnCl<sub>2</sub>·4H<sub>2</sub>O (10.1 mg, 0.051 mmol), TbCl<sub>3</sub>·6H<sub>2</sub>O (1 eq., 19.2 mg, 0.051 mmol) and **H45** (50.6 mg, 0.052 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et<sub>3</sub>N (0.045 mL) was added and the resulting purple solution was stirred at RT for 2 hours. The reaction mixture was filtered to remove any microcrystalline material, and purple crystals of **7** grew upon vapour diffusion of petroleum ether into the mother liquor. These were found to be sensitive towards solvent loss upon removal of the mother liquor, and sample homogeneity was assessed by multiple unit cell determinations. **Crystal data for 7 (CCDC 1583897):** C<sub>148.25</sub>H<sub>185.75</sub>Mn<sub>4</sub>N<sub>6.75</sub>O<sub>25</sub>, *M* = 2682.03 g/mol, triclinic, space group *P*-1 (no. 2), *a* = 15.7886(9) Å, *b* = 23.1399(13) Å, *c* = 30.3907(17) Å, *α* = 102.631(3)°, *β* = 102.128(3)°, *γ* = 98.886(3)°, *V* = 10356.2(10) Å<sup>3</sup>, *Z* = 2, *T* = 100(2) K,  $\mu$ (synchrotron) = 0.361 mm<sup>-1</sup>, 111410 reflections measured (3.224° ≤ 2 $\Theta$  ≤ 62.414°), 51084 unique (*R*<sub>int</sub> = 0.0495, *R*<sub>sigma</sub> = 0.0784) which were used in all calculations. The**

final  $R_1$  was 0.0806 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2422 (all data).

**Synthesis of [Tb<sup>III</sup><sub>6</sub>( $\mu_4$ -O)<sub>2</sub>( $\mu_4$ -CO<sub>3</sub>)<sub>2</sub>( $\mu$ -HCO<sub>2</sub>)<sub>2</sub>(**5**)<sub>2</sub>(dmf)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>](MeOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, **8**:**

MnCl<sub>2</sub>·4H<sub>2</sub>O (10.1mg, 0.051 mmol), TbCl<sub>3</sub>·6H<sub>2</sub>O (4 eq., 76.7 mg, 0.205 mmol) and **H45** (50.6 mg, 0.052 mmol) were dissolved in a 1:1 DMF/MeOH mixture (20 mL). After 10 minutes of stirring Et<sub>3</sub>N (0.045 mL) was added and the resulting purple solution was stirred at RT for 2 hours. The reaction mixture was filtered to remove any microcrystalline material, and colourless crystals of **8** grew upon slow evaporation of the mother liquor. These were found to be sensitive towards solvent loss upon removal of the mother liquor, and sample homogeneity was assessed by multiple unit cell determinations. **Crystal data for 8 (CCDC 1583898):** C<sub>79</sub>H<sub>105</sub>N<sub>4</sub>O<sub>21</sub>Tb<sub>3</sub>,  $M = 1923.42$  g/mol, monoclinic, space group  $P2_1/n$  (no. 14),  $a = 18.8372(9)$  Å,  $b = 15.8997(8)$  Å,  $c = 28.3456(12)$  Å,  $\beta = 107.806(2)^\circ$ ,  $V = 8083.0(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 100(2)$  K, MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), 72883 reflections measured ( $3.45^\circ \leq 2\theta \leq 58.082^\circ$ ), 21054 unique ( $R_{\text{int}} = 0.0847$ ,  $R_{\text{sigma}} = 0.1167$ ) which were used in all calculations. The final  $R_1$  was 0.0527 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1354 (all data).

## 5. Disclosure Statement

The authors declare no conflicts of interest.

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