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A New Family of 3d-4f Bis-Calix[4]arene-Supported Clusters


Abstract: Calix[4]arenes are versatile ligands that, whilst also serving other purposes, can act as platforms for the synthesis of a wide range of 3d, 4f and 3d–4f polymetallic clusters. The empirical metal ion binding rules established for calix[4]arene are closely mirrored by bis-calix[4]arene, a relatively new ligand in which two equivalents of the former are directly tethered at a methylene bridge position. The direct tethering within bis-calix[4]arene gives rise to some structural features that are related to calix[4]arene coordination chemistry, but the prevailing clusters have fascinating new topologies and coordination behaviors. Here we present the synthesis of a family of new bis-calix[4]arene-supported 3d–4f clusters, as well as their structural characterization and magnetic properties. Comparison is drawn with calix[4]arene coordination chemistry, showing logical extension of common structural fragments and cluster capping behaviors upon moving to bis-calix[4]arene. This approach therefore holds great potential for tuning cluster formation and composition at a high level through subsequent ligand alteration.

Introduction

The synthesis of complex metallosupramolecular assemblies / polymetallic clusters can be achieved via several strategies that range from serendipitous formation through to directed assembly. The latter, that can alternatively be termed rational design, typically relies on the synthesis of ligands or building blocks that possess particular structural characteristics and / or chemical functionalities.[10] These properties subsequently allow the chemist to employ specific metal ion binding modes in order to impart topologically directing character, representing a generally preferred route towards the isolation of challenging multi-component assemblies. This approach can also be used to control and / or tune the chemical and physical properties[10] of the resulting assembly by exerting strong influence over cluster composition. The result of such control is the generation of new polymetallic clusters that are well understood and that have potential application in many areas of research; examples include their use as Single Molecule Magnets (SMMs),[9] catalysts[4] and host-guest systems.

Calix[4]arenes (general notation C[4] hereafter) have been used widely in supramolecular chemistry, the reasons for which include their possessing interesting conformational properties, the ease with which one can synthetically modify the upper- and / or lower-rims,[9] their propensity to act as hosts for suitably sized guests, and the fact that the polyphenolic lower-rim can bind 3d / 4f metal ions and form polymetallic clusters through phenolate bridging.[9] We (amongst others) have been actively exploring C[4] lower-rim coordination chemistry and related cluster formation, and in doing so have established an extensive library of 3d, 4f and 3d–4f clusters.[7] Our first result in this area was the synthesis of a series of [MnII3,MnII2(OH)2(C[4])]4+ SMMs displaying the common butterfly-like (MnII3MnII2(OH)2) core (Fig. 1A),[8] but with the oxidation state distribution reversed relative to the majority of analogous cluster core topologies found in the literature.[9] In this cluster type the body Mn cations are in a 2+ oxidation state, whereas those bound by the C[4] tetraphenolic pocket are in a 3+ oxidation state and occupy the wing-tip positions. The wing-tip [MnII3(C[4])]4+ moiety caps the cluster core on each side, and this is in fact a recurring feature in C[4]-supported coordination chemistry; to date we have found that [TMI2(C[4])]4-, [TMI2(C[4])2-] or [LnIII(C[4])]4+ moieties act as capping vertices, with C[4] oxygens bridging to metal ions within the cluster core.

We recently found that it is possible to replace one or both of the body MnIII ions in the aforementioned cluster with LnIII ions through variation in the metal salt, stoichiometries and reaction conditions employed; this afforded structurally related butterflies having {MnII3,MnII3LnIII3(OH)2} and {MnII3,LnIII2(OH)2} cores respectively.[10] Analogous reactions carried out in the absence of TMI2 ions afforded C[4]-supported LnIII octahedra,[11] and a series of MnII4LnIII4 clusters (Fig. 1B) were also obtained when both TM and Ln ions.[12] The latter are best described as a square of LnIII ions capped on each edge by four [MnII3LnIII(C[4])]4+ moieties, and these behave as SMMs or molecular refrigerants depending on the lanthanide employed. Finally, treatment of C[4] with copper(II) nitrate trihydrate afforded enneanuclear clusters (Fig. 1C) that have a tri-capped trigonal prismatic topology.[13] These clusters display interesting versatility in anion binding within the trigonal prismatic core, and [CuI4(C[4])3]+ moieties cap each face of the polyhedron. Analysis of this library of clusters has allowed us to establish metal ion binding rules for C[4] as follows: 1) MnIII is preferentially bound over other TM and Ln ions; 2) TMII ions (e.g. CuI) are preferentially bound over LnIII ions in the absence of TMIII ions (e.g. MnIII); 3) LnIII ions will be bound in the absence of both TMIII and TMII ions.[14] With these rules in mind, we recently began investigations into cluster formation with bis-p-Bu-calix[4]arene (bis-C[4]), a relatively new ligand comprising two C[4]s directly linked via the methylene bridge.[15] This is of particular interest considering that, akin to C[4], bis-C[4] would be conformationally flexible, but it could also act as a double capping species upon complexation.

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with suitable metal ions. Initial investigations conducted with bis-C[4] showed that the established binding rules were indeed maintained upon metal ion complexation, and the first cluster isolated was a \([\text{Mn}^{III}\text{Mn}^{II}(_{\text{bis-C}[4])}]\) species that can be visualized as two distorted and fused \([\text{Mn}^{III}\text{Mn}^{II}]) cores (compare Fig. 1A and 1D). Structural differences between these two related clusters are primarily due to methylene bridge linking, and in this case two Mn ions occupy binding sites between the two C[4] moieties. In this regard, it should be noted that the free ligand exists as an up-down antiparallel arrangement of C[4] (Fig. S1), and inversion gives rise to these new metal ion binding sites between their polyphenolic lower-rims. As is the case for \([\text{Mn}^{III}\text{Mn}^{II}(_{\text{OH}})]\); the \text{Mn}^{III} ions in the bis-C[4]-supported cluster are linked through bridging phenolates and hydroxides. The second cluster to emerge from this exploratory chemistry was a \([\text{Mn}^{III}\text{Mn}^{III}\text{Gd}^{III}(_{\text{bis-C}[4])}]\) species that is a structural relative of the aforementioned Mn2 cluster (compare Fig. 1D and 1E); the main difference being the interchange of two Mn3+ for Ln3+ ions; this behavior is a close parallel to that described above for C[4].

Exploration of this variable led to the isolation of two new clusters, \([\text{Mn}^{III}\text{Mn}^{III}\text{Gd}^{III}(_{\text{bis-C}[4])}]\) and \([\text{Mn}^{III}\text{Mn}^{III}\text{Gd}^{III}(_{\text{bis-C}[4])}]\), the cores of which have been ‘expanded’ through the incorporation of two additional central Mn3+ ions in each case relative to their \([\text{Mn}^{III}\text{Mn}^{III}(_{\text{bis-C}[4])}]\) and \([\text{Mn}^{III}\text{Mn}^{III}\text{Gd}^{III}(_{\text{bis-C}[4])}]\) relatives respectively.

Given the structural trends observed upon moving from C[4] to bis-C[4], it is clear that the metal ion binding rules established for the former translate to the latter. Here we report the isolation, characterization and magnetic properties for three new \([\text{TM}^{III}\text{Ln}^{III}(_{\text{bis-C}[4])}]\) clusters incorporating either CuII, FeIII or MnIII ions, representing a significant addition to the library of known cluster types with this ligand. The established binding rules again translate for these metal ions, further suggesting that the linkage of calix[n]arenes of varying ring size represents a burgeoning area of research for investigation.

**Results and Discussion**

Reaction of bis-C[4] with copper(II) and terbium(III) nitrate hydrates in a DMF / MeOH mixture (to aid bis-C[4] solubility) and in the presence of Et3N as a base afforded single crystals of formula \([\text{Cu}^{II}\text{TB}^{III}(_{\text{bis-C}[4])}_2\text{MeOH}\text{MeOH}][\text{Mn}^{III}\text{Mn}^{III}\text{Gd}^{III}(_{\text{bis-C}[4])}]\). We recently showed that, as in C[4]-supported cluster chemistry, variation in reaction stoichiometry has a dramatic effect on the assembly of bis-C[4]-supported clusters. Further suggesting that methylene bridge linking is a viable route to the logical extension of metal ion binding rules / behaviors for multi-component systems.
the space group P2₁/n. The asymmetric unit comprises two bis-C[4]s housing a Cu₅[Tb₄]₅ metallic core, the cations in which are bridged by hydroxide and nitrate anions (Fig. 2). The four CuⅡ ions are located in the fully deprotonated lower-rim bis-C[4] phenolato pockets (Cu–O bond lengths in the range of 1.906(7) – 2.031(7) Å) and their coordination spheres are completed by μ₂-hydroxide, μ₂-methoxide and μ₄-nitrate anions (Cu–O bond lengths in the range of 2.202(7) – 2.239(7) Å). These anions bridge to the five TbⅢ ions (Tb–O bond lengths in the range of 2.260(7) – 2.494(7) Å), four of which are seven coordinate (distorted pentagonal bipyramidal geometries) and are located in the binding sites generated by inversion of the bis-C[4] ligands. The remaining TbⅢ ion (Tb3) is octacoordinate, has distorted square antiprismatic geometry and links the two [Cu₅[Tb₄](bis-C[4])] fragments, and is located near-equidistant from these two moieties; the distances found between Tb3 and the centroids generated by each [Cu₅[Tb₄](bis-C[4])] fragment are both ~4.7 Å. All of the TbⅢ ions are bound to the aforementioned bridging anions, bis-C[4] oxygens (Tb–O bond lengths in the range of 2.279(6) – 2.385(7) Å) and ligated solvent molecules (dmf, MeOH or H₂O, with Tb–O bond lengths in the range of 2.304(7) – 2.397(8) Å). Double capping behavior is observed as anticipated, in this case with two [Cu₅(bis-C[4])]₄ moieties encapsulating two TbⅢ cations residing within the binding pockets originating from ligand inversion (Fig. 2B). Symmetry expansion of the structure of 1 does not show any significant interaction between the metal clusters, and co-crystallized dmf molecules occupy space between symmetry equivalents (s.e.) along the a and c axes. The closest metal-metal intercluster distance is along the b axis and is ~12.9 Å between Cu1 and Cu4 of a s.e. cluster (Figure S2).

Treatment of bis-C[4] with iron(III) and gadolinium(III) nitrate hydrates in a DMF / MeOH mixture in the presence of Et₃N as a base afforded single crystals of formula [Fe₃III,GdIII(bis-C[4])₂(µ₂- O)(µ₂-O)(µ₂-NO₃)(dmf)(H₂O)](OH), 2, upon slow evaporation of the mother liquor. The crystals were found to be in a triclinic space group and structure solution was carried out in the space group P-1. The asymmetric unit comprises a distorted FeIII,GdIII butterfly housed within a bis-C[4], and a FeⅡ ion linked to the aforementioned butterfly via bridging nitrate and oxo anions. Symmetry expansion around the inversion center gives rise to the whole cluster shown in Figure 3A. As can be seen by inspection, two [FeIII,GdIII(bis-C[4])] butterflies / fragments are linked by the near-central FeⅡ cation that sits just away from the aforementioned center of inversion, located between the two cluster fragments. This FeⅡ ion and the bridging nitrates are disordered over two positions (one position shown in Fig. 3A) and this disorder was successfully modelled using partial occupancies; only one position is discussed here for the sake of brevity.

![Figure 2. Views of the single-crystal X-ray structure of 1 showing the polymeric Cu₅[Tb₄] core. A) Two butterfly fragments linked through a central TbⅢ ion and bridging nitrates. B) Metallic skeleton of 1 with the capping [Cu₅[Tb₄]]₄ moieties drawn as large spheres. The view in B is a 90° rotation of A. Bis-C[4] Bu groups, H atoms and ligated solvent molecules omitted for clarity. Colour code: Cu – light blue, Tb – green, C – grey, N – blue, O – red.](image1)

![Figure 3. Views of the single-crystal X-ray structure of 2 showing the polymeric Fe₃III,GdIII core. A) Two butterfly fragments linked through a central FeⅡ ion and bridging nitrates/oxides. B) Metallic skeleton of 2 showing edge capping by [FeⅡ(TBC][4])] moieties (drawn as large spheres), GdIII ions arranged in a square and face capping by the central FeⅡ ion. Bis-C[4] Bu groups, H atoms and ligated solvent molecules omitted for clarity. Colour code: Fe – dark blue, Gd – green, C – grey, N – blue, O – red.](image2)
Fe1, Fe2, and their symmetry equivalents are all hexacoordinate, have distorted octahedral geometries, and reside in the fully deprotonated lower-rim bis-C[4] phenolato pockets (Fe–O bond lengths in the range of 1.95(4) – 2.02(4) Å); this is expected based on the metal ion binding rules outlined in the introductory section. The Fe1 / Fe2 coordination spheres are completed by ligated dmf molecules that reside in the bis-C[4] cavities (Fe1–O11, 2.091(8) Å and Fe2–O12, 2.108(6) Å) and μ-III anions (Fe1–O9, 1.942(6) Å and Fe2–O10, 1.938(5) Å) that bridge to Gd1 and Gd2 (Gd–O bond lengths in the range of 2.375(2) – 2.403(6) Å). Both Gd1 and Gd2 are octacoordinate, have distorted square antiprisms, and are located in the binding pockets generated by bis-C[4] inversion. Each GdIII ion is bound to two bis-C[4] oxygen atoms (Gd–O bond lengths in the range of 2.351(4) – 2.385(5) Å), two oxygen atoms of a μ-NO3 anion (Gd–O bond lengths in the range of 2.276(8) – 2.564(4) Å) and ligated solvent molecules (Gd–O bond lengths in the range of 2.356(7) – 2.572(12) Å). Finally, Fe3, located near the center of the cluster, bridges the two [Fe(III)Gd(III)]3(bis-C[4])2 butterflies / fragments as outlined above, and caps one face of the square described by the GdIII cations. The Fe3 coordination sphere is completed by two μ-III anions (Fe3–O10, 1.972(4) Å and Fe3–O9’, 2.039(5) Å), oxygens from two μ-NO3 anions (Fe3–O21, 2.247(5) Å and Fe–O21*, 2.265(5) Å) and two aqua ligands (Fe3–O16, 2.016(10) Å and Fe3–O17, 2.019(10) Å). The GdIII square is also capped on each edge by a [Fe(III)bis-C[4])2 moiety in line with the expected double-capping behavior of bis-C[4]; the capped GdIII square is also a recurring structural motif when considering previously reported C[4]-supported metal clusters, although in this case double capping occurs in an alternative manner around the central core.12 Symmetry expansion of the structure of 2 reveals weak Van der Waals interactions along the c axis between the dmf molecule ligated to Gd2 and its s.e.; this occurs with a distance between nitrogen atoms of ~3.7 Å. The closest metal-metal intercluster distances were also found along the c axis, occurring between Gd2 and its s.e. with a distance of ~11.2 Å. The next shortest metal-metal intercluster distance of note is between Fe3 and Gd2 from a s.e. cluster, occurring with a distance of ~13.9 Å (Figure S3).

Reaction of bis-C[4] with manganese(II) and gadolinium(III) chlorides in a DMF / MeOH mixture and in the presence of Et3N as a base afforded single crystals of formula [Mn4Gd4(bis-C[4])2(μ-OH)2(μ-CO)2(dmfb)(H2O)4][MeOH](dmf)2, 3, upon slow evaporation of the mother liquor. The crystals were found to be in a monoclinic cell and structure solution was carried out in the space group P21/n. The asymmetric unit comprises two distorted [Mn4Gd4(bis-C[4])2]2+ butterflies / fragments, and these are connected via carbonate bridges, likely resulting from fixation of atmospheric CO2; this is a common phenomenon in Ln coordination chemistry10 and has been previously reported in C[4]-supported cluster chemistry. The four MnII ions are in a distorted octahedral geometry and are located in the fully deprotonated lower-rim bis-C[4] phenolato pockets (Mn–O bond lengths in the range of 1.889(5) – 1.994(5) Å). Oxidation states were confirmed by bond valence sums (BVS), giving respective values of 3.16, 3.12, 3.32 and 3.08 for Mn1 – Mn4. Their coordination spheres are completed by ligated dmf molecules that reside in the C[4] cavities (Mn – O(dmf) bond lengths in the range of 2.152(6) – 2.239(5) Å and μ-OH anions that bridge each MnIII to the closest GdIII ion (Mn – O(μ-OH) bond lengths in the range of 2.002(5) – 2.130(4) Å); these ligands define the Jahn-Teller axis for each MnIII ion, details of which can be found in the supporting information (Figure S4). The four GdIII cations are octacoordinate, have square antiprisms, and reside in the binding regions generated by bis-C[4] inversion. Each GdIII cation is bound to two bis-C[4] oxygens (Gd–O bond lengths in the range of 2.331(5) – 2.523(5) Å), as well as ligated solvent molecules (Gd–O bond lengths in the range of 2.351(6) – 2.430(5) Å). These cations are bridged via the aforementioned μ-OH anions (Gd–O bond lengths in the range of 2.322(5) – 2.434(5) Å) and oxygen atoms of carbonate bridges that are linking the two halves of the cluster (Gd–O range 2.393(5) – 2.480(5) Å). The metallic core in 3 is different to that found in 2, perhaps due to the lack of a central bridging metal ion, and is best described as a distorted rectangle of LnIII ions, capped on the shorter sides by a [Mn4Gd4(bis-C[4])2]2+ moiety. Again, the observation of persistent structural trends suggests that one may link >2 C[4] via the methylene bridges to logically influence cluster formation and, potentially, the physical properties of the resulting assemblies.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Views of the single-crystal X-ray structure of 3 showing the polymeric MnII/GdIII core. A) Two butterfly fragments linked through bridging carbonates. B) Metallic skeleton of 3 with the capping [Mn4(TBC[4])2]2+ moieties drawn as large spheres, and showing the GdIII ions arranged in a square. Bis-C[4] "Bu groups, H atoms and ligated solvent molecules omitted for clarity. Colour code: Mn – purple, Gd – green, C – grey, O – red.
Symmetry expansion of the structure of 3 reveals that there are no significant intermolecular interactions occurring between the clusters. The shortest metal-metal intercluster distance is along the a axis, occurring between Gd1 and Gd4 of a s.e. cluster with a distance of ~12.8 Å (Figure S5). The second, comparable intercluster distance, occurs along the b axis between Mn2 and a s.e. Mn3 with a distance of ~13.0 Å.

**Magnetic properties**

The dc (direct current) molar magnetic susceptibility, $\chi_M$, of polycrystalline samples of 1-3 were measured in an applied magnetic field, B, of 0.1 T, over the $T = 5-300$ K temperature range. The experimental results are shown in Figure 5 in the form of the $\chi_M T$ product versus $T$, where $\chi_M = M / B$, and $M$ is the magnetisation of the sample. At room temperature, the experimentally observed $\chi_M T$ products of 60.8, 53.9 and 44.0 cm$^3$ K mol$^{-1}$ are consistent with the Curie constants for [Cu$_2$Tb$_n$], [Fe$_n$Gd$_{10}$] and [Mn$_{30}$Gd$_{20}$] units, respectively. Upon cooling, the $\chi_M T$ product of compound 1 remains relatively constant until $T \approx 175$ K where the it begins to decrease slowly, reaching a value of 46.9 cm$^3$ K mol$^{-1}$ at $T = 5$ K. The data for complexes 2 and 3 are rather different, both $\chi_M T$ products remaining constant until approximately $T = 50$ K wherefrom they increase to maximum values of 57 (2) and 53 cm$^3$ K mol$^{-1}$. The behaviour in all three cases is consistent with competing (weak) ferro- and antiferromagnetic exchange interactions, with the decrease in $\chi_M T$ in 1 associated with the depopulation of ligand-field sublevels of the Tb$^{3+}$ ion. The large nuclearities, complex topologies and the presence of the anisotropic Tb$^{3+}$ ion prevents quantitative analysis of the exchange constants in these compounds, but some general comments can be made. Inspection of the structures of 1 (Figure 2) and 3 (Figure 4) shows there are no direct, ligand-mediated $\text{TM} \cdot \cdot \cdot \text{TM}$ ($\text{TM} = $ transition metal) magnetic exchange pathways, only $\text{TM} \cdot \cdot \cdot \text{Ln}$ and $\text{Ln} \cdot \cdot \cdot \text{Ln}$ ($\text{Ln} = $ lanthanide metal) contacts, both of which would be expected to be very weak. Indeed, previous measurements of calix[n]arene-based TM$^{III}$-Gd$^{III}$ clusters reveal exchange constants that are just a fraction of a wavenumber, with the shape of the $\chi_M T$ versus $T$ curve for 3 being very similar to that observed for the C[4]-supported [Mn$_{30}$Gd$_{20}$] species, where $J_{\text{Mn-Gd}} = +0.075$ cm$^{-1}$ and $J_{\text{Gd-Gd}} = -0.006$ cm$^{-1}$.[10]

Analysis of the magnetic data of compound 2 is further complicated by the presence of the central Fe3 ion which is disordered over two positions. While reported Fe$^{III}$-Gd$^{III}$ exchange constants in C[4]-supported cages are of the same magnitude as described above,[14] Fe$^{III}$-O-Fe$^{III}$ exchange can be large, though strongly dependent on the Fe$^{III}$-O-Fe$^{III}$ angle, with the strongest AF exchange observed for a linear moiety and becoming less AF as the angle decreases.[20] The Fe$^{III}$-O-Fe$^{III}$ angles in 2 (Fe1-O9-Fe3: Fe3-O10-Fe2) are approximately 130° (with $\mu_2$-O9, $\mu_3$-O10 also bridging to two Gd ions), and inspection of Figure 5 suggests little evidence for the presence of strong TM$\cdot \cdot \cdot$TM exchange. These observations are also consistent with low temperature variable-temperature-and-variable-field (VTVB) magnetisation data collected in fields of up to $B = 7$ T (Figure 5). While the magnetisation (Figure 6) of complex 1 does not saturate at $B = 7$ T ($M = 26.4 \mu_B$), those for complexes 2 ($M = 48.0 \mu_B$) and 3 ($M = 41.6 \mu_B$) are approaching that expected for the field-induced stabilisation of the maximum $S = 53/2$ and $S = 22$ states, respectively. There are no frequency-dependent signals in out-of-phase ($\chi_M$) ac susceptibility for 1-3, ruling out any SMM behaviour.

![Figure 5](image_url) **Figure 5.** Plot of $\chi_M T$ versus $T$, for complexes 1-3 in a field of $B = 0.1$ T.

![Figure 6](image_url) **Figure 6.** Plot of magnetisation ($M$) versus field ($B$) for complexes 1-3 at $T = 2$ K.

**Conclusions**

In conclusion, our library of bis-C[4]-supported metal cluster has been significantly expanded in this contribution through the synthesis and characterization of three novel assemblies. Dc susceptibility and magnetization measurements reveal the presence of competing (and weak) ferro- and antiferromagnetic interactions in all three cases, consistent with the behavior of similar cages constructed with C[4]. Despite the complexity of the systems reported, the coordination modes observed / cluster topologies obtained are fully compliant with anticipated structure capping behavior, suggesting that further and logical extension of
ligand design principles should lead to the isolation of tailored, highly symmetric, high nuclearity clusters that will be of interest to many. Work continues with this goal in mind, but also with a view to understanding the influence of co-ligands on cluster formation with bis-C[4]. Results from these studies will be reported in due course.

Experimental Section

Bis-C[4] was synthesized according to literature procedure.\cite{10} Single crystal diffraction data were collected on a Bruker APEX II CCD diffractometer equipped with a PHOTON 100 detector operating at 100(15) K and using synchrotron radiation (λ = 0.7749 Å). Supporting information includes a figure showing the structure of bis-C[4], as well as videos showing rotating structures for 1 – 3.

Synthesis of [(Cu\textsubscript{4}Tb\textsubscript{4}Cl\textsubscript{4})\textsubscript{2}][μ-OMe][μ-OMe][μ-OH][μ-NO\textsubscript{3}][μ-NO\textsubscript{3}][μ-NO\textsubscript{3}][μ-HO][μ-O][μ-CO\textsubscript{2}][μ-H]\textsubscript{2}]2\{H\textsubscript{2}O\}2, 1: BisTBC[4] (350 mg, 0.27 mmol, 1 eq.) and Tb(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (245 mg, 0.54 mmol, 2 eq.) were suspended in a 1:1 DMSO/MeOH mixture (20 mL) and stirred for 10 minutes. Ethanol (0.35 mL) was added and the resulting orange solution was stirred for an additional 2 h and filtered. The mother liquor was allowed to slowly evaporate, affording crystals suitable for X-ray diffraction studies. Elemental Analysis (%) calculated for 1, C\textsubscript{27}H\textsubscript{30}Cu\textsubscript{4}Tb\textsubscript{4}Cl\textsubscript{4}N\textsubscript{2}O\textsubscript{4} (M = 19,782.72): C, 56.44%; H, 6.57%; N, 3.15%.

Crystal data for 3 (CCDC 1560944): C\textsubscript{32}H\textsubscript{42}Gd\textsubscript{6}Mn\textsubscript{11}N\textsubscript{2}O\textsubscript{24}L\textsubscript{4}, M = 45,565.94. Purple needle, 0.3 x 0.07 x 0.01 mm\textsuperscript{3}, monoclinic, space group P2\textsubscript{1}/n (No. 14), a = 17.7206(8), b = 41.6212(17), c = 33.0584(14) Å, β = 102.014(2)º, V = 23848.3(18) Å\textsuperscript{3}, Z = 4, 2\textsubscript{max} = 54.448º, 40,784 reflections collected, 40,784 unique (R\textsubscript{int} = merged, R\textsubscript{free} = 0.0524). Final GoF = 1.085, R\textsubscript{1} = 0.0690, wR\textsubscript{2} = 0.1785.

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Keywords: Calixarenes • Clusters • Coordination Chemistry • Magnetism • Coordination Modes


Bis-calix[4]arene is a versatile ligand that have been used to form a new family of 3d–4f polymetallic clusters. Empirical metal ion binding rules established for calix[4]arene are closely mirrored in this ligand, suggesting that one may use coordination preferences and ligand alteration / design in order to tune both cluster formation and composition at a high level in complex multi-component systems.