Facile interchange of 3d and 4f ions in single-molecule magnets: Stepwise Assembly of [Mn4], [Mn3Ln] and [Mn2Ln2] Cages within Calix[4]arene Scaffolds

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Abstract: The central Mn²⁺ ions in a series of calix[4]arene-stabilised butterflies can be sequentially replaced with Ln³⁺ ions, maintaining the structural integrity of the molecule but transforming its magnetic properties. The replacement of Mn⁸⁺ for Gd⁸⁺ allows for the examination of the transferability of spin-Hamiltonian parameters within the family as well as permitting their reliable determination. The introduction of the 4f ions results in weaker intramolecular magnetic exchange, an increase in the number of low-lying excited states, and an increase in magnetisation relaxation, highlighting the importance of exchange over single-ion anisotropy for the observation of SMM behaviour in this family of complexes. The presence of the [TM₁³⁺(TBC₄)(OH)(solvent)] metalloligand suggests that magnetic calix[n]arene building blocks can be employed to encapsulate a range of different “guests” within structurally robust “hosts”.

Introduction

Polymetallic clusters containing paramagnetic metal ions have emerged as promising candidates for a variety of potential technological applications, stemming from their inherently interesting and potential useful low temperature physics.[1-9] Single-Molecule Magnets (SMMs)[1] in particular have been touted for use in areas such as molecular spintronics and information storage.[2-9] Application first requires understanding of the structure-magnetism relationship and this, in turn, is reliant upon synthetic coordination chemistry and the systematic exploration of the reaction conditions required to build families of related compounds, which thereafter can be exploited to fine tune properties through subtle changes to structure.[10]

In a series of experiments we (amongst others) have shown that methylene-bridged calix[n]arenes (C[n]s) can act as versatile ligands for the construction of polynuclear transition metal (TM),[11] lanthanide/rare earth metal (LnM)[12] and 3d-4f clusters.[13] The most suitable C[n] supports in this regard are closely related p-Bu-calix[4]arene and calix[4]arene (TBC[4] and C[4], respectively), a feature stemming from the fact that they reliably coordinate to a TM or LnM so that it lies centrally within the polyphenolic binding cavity of the cone-shaped ligand (Fig. 1A). Empirical binding rules established from our library of reactions and structures shows the preference TM > LnM, presumably a simple result of better size-matching. The lower-rim phenolic oxygen atoms are capable of bridging to additional metal ions that occupy well-defined and [somewhat] predictable positions based on the cone shape of the ligand. Analysis of the common structural features in the TBC[4]-supported clusters we have isolated to date shows that whether the calixarene binds a TM or TM III ion, the hydrophobic upper cavity is occupied by a ligated solvent molecule (typically DMF or DMSO) and the O-atoms of the fully deprotonated lower-rim, in conjunction with a bound hydroxide ligand beneath the complex, act as bridges to other metal centres. The common building block or “metalloligand” seen in all [our] TBC[4]-supported TM clusters is thus [TM₁³⁺(TBC₄)(OH)(solvent)] (Fig. 1B). This is of course particularly suited to the Jahn-Teller distorted Mn⁸⁺ and Cu²⁺ ions since the fully deprotonated calix[4]arene is predisposed to house metal ions preferring four short equatorial and two long axial bonds.

Results and Discussion

We previously reported that the reaction between a Mn²⁺ salt and TBC[4] in a basic MeOH/DMF solution results in the formation of [Mn⁸⁺₂Mn⁷⁺₂(OH)₂(TBC₄)₂(DMF)₆] (1, Fig. 2A).[11b,c] The complex contains a [Mn⁷⁺₂Mn⁵⁺₂(µ₂-OH)₂]⁴⁺ core that possesses a planar butterfly-like topology, with the Mn⁸⁺ ions housed within the calixarene (O₂) cavity at the wing-tip positions, and the Mn⁸⁺ ions “sandwiched” in the central body positions. The structure of 1 can be regarded rather simply as two [Mn⁷⁺₃(TBC₄)(OH)(DMF)]⁶⁻ moieties that have encapsulated two additional “naked” Mn⁸⁺ ions.
whose remaining coordination sites are occupied by solvent, and from a synthetic perspective this raises an intriguing question: can these encapsulated “naked” metal ions be replaced / swapped whilst maintaining the structural integrity of the complex? Herein we show that indeed this is the case, and that the family can be expanded to include heterometallic clusters in which LnIII ions are added to the central body positions to form both [MnIII2LnIII(Ln)]2+ and [MnIII3LnIII(Ln)]3+ complexes.

For each cluster type ([MnIII2MnIII(Ln)(TBC[4])]2+ and [MnIII3MnII(TBC[4])]3+) there exists several examples that can be made in a variety of ways, and so for the sake of brevity only a generic structure description of each type will be given. Full details of reaction conditions (Table S1) and structures (Fig. S1) are listed in the Supporting Information, and only combinations that afforded phase pure material with unambiguous crystallographic assignments of different metal positions are included. Reaction of Mn(NO3)2·4H2O, LnM(NO3)3·6H2O and TBC[4] in a basic mixture of dmos:EtOH followed by slow diffusion with MeCN vapour afforded a series of clusters of general formula [MnIII2LnIII(Ln)(OH)2(TBC[4])2(NO3)(solvent)6], (LnM = Y, Gd, Tb, Dy, Ho, with the Gd analogue, 2, shown in Fig. 2B). We also found that a dmf:EtOH solvent combination followed by slow diffusion with PrOH gave the same general cluster motif with formula [MnIII2MnII(Ln)(OH)2(TBC[4])2(NO3)(dmf)4(PrOH)2] (LnM = Gd, Dy), with dmf / PrOH occupying the analogous positions to dmso in 2. Cluster 2 is comprised of a butterfly-like {MnIII2MnII(Gd)(OH)2} core that is entirely analogous to that of 1 (Fig. 2A), but with one MnII ion replaced with a LnIII ion. As expected the wing-tip Mn ions, housed within the calixarene O4 pockets, are in the +3 oxidation state, whilst the MnIII and GdIII ions occupy the central body positions. The Jahn-Teller axes of the MnIII ions are defined by the OH-Mn-solvent(dmso) vectors (four Mn-O distances in the range of 2.130(7) – 2.467(15) Å), and deviate slightly from linearity (164 – 165°). The four equatorial sites of each MnIII ion are occupied by TBC[4] phenolic oxygen atoms (eight Mn-O distances in the range of 1.888(7) – 1.981(7) Å). Two of these O atoms bridge further to the central TMII and GdIII ions (two O-Mn and two O-Gd distances with respective values of 2.212(7) / 2.190(7) Å and 2.371(7) / 2.371(7) Å). The GdIII ion exists in a distorted square antiprismatic geometry with its coordination sphere completed by two dmos ligands, a bidentate nitrate anion, and two µ3-hydroxides; the latter connect its coordination sphere completed by two dmso ligands, a bidentate nitrate anion, and two µ3-hydroxides; the latter connect its coordination sphere completed by two dmso ligands.

A comparison of the full structure of 1 with 2 (compare Fig. 2A and 2B) reveals that the presence of the larger lanthanide ion in the latter skews the relative orientations of the two TBC[4] ligands. In 1 the TBC[4]s are co-planar, whilst in 2 they present a slightly more clam-shell / pacman like appearance with the two O4 planes forming an angle of ~7° with respect to one another. There is a marked change in the angles between the constituent metal centres upon moving from 1 to 2, and the MnIII...MnIII distance is found to increase from 5.7743(15) to 5.812(7) Å (Fig. 2). Examination of the extended structure in 2 reveals assembly in a bilayer arrangement (Fig. S2) akin to that of the [MnIII2MnII(TBC[4])]2+ SMM and various TBC[4] solvates, and as such nearest neighbours are well isolated, with the closest metal-metal distances being of the order of 9.4 Å within layers and 14.6 Å between layers.[11c-e]

A second type of butterfly-like cluster was selectively isolated through the use of different reaction conditions: reaction of MnCl2·4H2O, LnMCl3·6H2O and TBC[4] in a basic mixture of dmos:MeOH followed by slow diffusion with PrOH vapour afforded an isostructural series of cages of formula [MnIII3LnIII(OH)2(TBC[4])2(dmso)4(iPrOH)2] (LnM = Y, Gd, Tb, Dy, Ho, with the Gd analogue, 3, shown in Fig. 2C).

![Figure 2. Molecular structures of 1 – 3 (A to C, respectively) with enlarged polymetallic cores shown for each structure.[11c-e] Key butterfly core parameters are listed to further highlight the structural changes upon sequential intercalation of GdIII for MnII ions. Hydrogen atoms and counter anions (3) omitted for clarity. Colour code: Mn, pale blue; GdIII, green; C, grey; O, red; N, royal blue; S, purple.](image-url)
presence of the nitrate ion was critical in the formation of 2, here it appears that the solvent mixture (dmsos/MeOH) is dominant, since a variety of metal salts (including halides and nitrates) can be employed. The metallic skeleton of 3 (Fig. 2C) is related to 1 via the exchange of both MnI ions for GdII ions. In the main, the structures of 2 and 3 are analogous, with the only major difference being in the coordination number and geometry of the GdII ions: here they are seven coordinate and in distorted pentagonal bipyramidal geometries, possessing three terminally bonded dmsos ligands (Gd-O range 2.308(3) – 2.358(3) Å). The introduction of two LnMII ions has re-introduced a co-planar arrangement of the O4 planes of the calix[4]arenes, and the MnIII...MnIII distance shows a further increase from 5.812(7) to 5.9148(12) Å. Cluster 3 is now cationic in contrast to neutral 1 and 2, with chloride counterions maintaining charge balance. The cages again assemble into bilayers as shown in Figure S3, with an interlayer spacing similar to that found in 2 and closest metal-metal distances between layers of 14.1 Å. The chloride counterions reside between adjacent clusters within the layers with a closest metal-metal distance of 10.7 Å. Inspection of 1 – 3 shows that the cluster core is becoming longer and wider upon the sequential exchange of MnIII for GdIII ions.

Despite the prevalence of butterfly-like structural motifs in polynuclear complexes, a search of the Cambridge Structural Database (CSD) returned only three entries for the general formula {MnIII2LnMII}, all of which differ in structure to 1. A more general search for the (TMnIILnM) butterfly core returned zero entries. A similar search for {MnIII2LnMII} butterflies returned 11 entries, but in each case the positions of the constituent ions were reversed from that observed in 2. Both searches highlight the structural novelty found in 1-3.

The exchange of MnII for GdIII ions upon moving from 1 – 3 provides the perfect opportunity to study the transferability of spin-Hamiltonian parameters within this family of compounds, as well as permitting reliable determination of the value of these parameters. The d.c. molar magnetic susceptibilities, , of polycrystalline samples of complexes 1 – 3 were measured in an applied magnetic field, B, of 0.1 T, over the 5 - 300 K temperature, T, range. The experimental results are shown in Fig. 3a in the form of products, where is the magnetic moment of MnII. The values of 15.5, 18.45 and 21.80 cm3 mol−1 K−1, respectively. For 1, this value is lower, but quite close, to that expected from the spin-only contributions for a [MnII] unit (14.75 cm3 mol−1 K−1), with , where is the g-factor of MnII. This is indicative of non-negligible exchange interactions operating in 1. For 2 and 3, the room temperature values of the products are quite similar to that expected from the spin-only contributions for a [MnIII2GdII] species (18.25 cm3 mol−1 K) and a [MnIII2GdIII] moiety (21.75 cm3 mol−1 K), respectively, with , respectively. This is indicative of weaker exchange interactions operating in 2 and 3, as one might expect following the introduction of one and two 4f ions. Upon cooling, the products for all three complexes increase slowly with decreasing temperature reaching 16.45 cm3 mol−1 K at 100 K for 1, 19.40 cm3 mol−1 K at 50 K for 2, and 22.45 cm3 mol−1 K at 30 K for 3. Further cooling results in a faster increase of the products, reaching 24.50, 22.90 and 23.20 cm3 mol−1 K, respectively. The products values expected from spin-only contributions to thermally isolated ground spin-states of ferromagnetically coupled [MnII2MnIII], [MnII2MnIII2GdII] and [MnII2GdIII2] units, would be 45.0, 55.0 and 66.0 cm3 mol−1 K, respectively. These results suggest the presence of both weak ferromagnetic and weak antiferromagnetic exchange interactions.

In order to better determine the low temperature energy spectra of 1 - 3, low temperature variable-temperature-variable-field (VTVB) magnetisation data were measured in the temperature range 2 - 7 K, in magnetic fields from 0.5 to 7.0 T. These data are shown in Figs 3b-d, where one can see that none of the three complexes reaches the saturation magnetic moment expected for a ferromagnetically coupled molecule. The magnetisation of 1 presents significant nesting, indicative significant magnetic anisotropy, which appears larger than that observed for 2 and 3, with the latter exhibiting the least anisotropy. Given that both MnII and GdIII are relatively magnetically isotropic, the difference in nesting in the VTVB data can likely be attributed to the larger magnitude of the total spin of GdIII (S = 7/2) as compared to that of MnII (S = 5/2).

To quantitatively interpret the magnetic properties of 1 – 3, we used the following general type of spin-Hamiltonian (1):

\[ H = \sum_i D_i (\hat{S}_i^2 - \frac{1}{3} \cdot (\hat{S}_i + 1)/3) + \mu_B \sum_j g_j \hat{S}_j - \sum_{i,j} J_{ij} \hat{S}_i \hat{S}_j \]  

where the summation indices i, j run through the constitutive metal centres, D is the uniaxial single-ion anisotropy parameter, is a spin operator, S is the total spin and J is the isotropic exchange interaction parameter. Given the structural differences between complexes 1 - 3, the parameters entering spin-Hamiltonian (1) for each of the complexes could in principle be different. However, interpretation of the experimental  and VTVB magnetisation data with such a large number of free parameters would most likely be of limited significance due to over-parameterisation. Thus, we attempted to fit the available experimental data by using transferable spin-Hamiltonian parameters between complexes 1 - 3. Thus, the model that we used contained the following free parameters: }.
These eigenvectors are significantly admixed, permitting numerous thermal relaxation pathways for magnetisation relaxation. Indeed, dynamic susceptibility measurements on 1 showed a nonzero out-of-phase ($\chi''$) component only at the highest frequencies and lowest temperatures investigated.\textsuperscript{11b,c} For 2, the ground-spin state of the isotropic part of spin-Hamiltonian (1), with the determined best-fit parameters, is an $S = 3$ state, and for 3 it is the ferromagnetic $S = 11$ state (Fig. 4) in both cases the ground states again lie in very close proximity to several excited spin-states, as in the case of 1. However, in 2, many more eigenstates (200) are located in the same energy window (20 cm$^{-1}$), and for 3 approximately 200 eigenstates are located within just the first 5 cm$^{-1}$. This of course is a direct consequence of the weak exchange mediated by the Ln ions. As we move from 1 to 2 to 3 we remove two and four ferromagnetic exchange interactions (Mn$^{III}$-Mn$^{II}$), which in the context of this molecule are relatively strong interactions, and replace them with two (2) and four (3) very weak ferromagnetic interactions that are more than an order of magnitude smaller. We also replace the AF Mn$^{III}$-Mn$^{II}$ interaction with the weaker AF Mn$^{III}$-Gd$^{III}$ interaction and yet weaker AF Gd$^{III}$-Gd$^{III}$ exchange. Thus, the conversion of the exchange-coupled Mn$^4$ towards the near paramagnetic Mn$^2$Gd$^2$ results in the presence of many more magnetisation relaxation pathways, as reflected in the appearance of diminishing signals (1→3) in out-of-phase ac susceptibility ($\chi''$) measurements (Fig. S7-S8). Indeed no $\chi''$ component is observed for 3, even at the highest frequencies (1000 Hz) and lowest temperatures (1.8 K) investigated.

On moving from [Mn$_3$Gd] to [Mn$_3$Tb] (2Tb) and [Mn$_3$Dy] (2Dy) the $\chi T$ data (Figure S9) are broadly similar – a high temperature plateau, followed by a low temperature increase in $\chi T$ - suggesting the same/similar exchange interactions are present in all three complexes. However, the data for the [Mn$_2$Ln$_2$] (Ln = Dy (3Dy), Tb (3Tb)) family members are rather different to the parent Gd complex, whereby the low temperature region witnesses a sharp decline in $\chi T$ rather than a small increase (Figure S10). This perhaps suggests the Dy/Tb-Mn$^{III}$ interaction to be weakly antiferromagnetic in contrast to the weakly ferromagnetic Gd-Mn$^{III}$ interaction.

Interestingly the replacement of the isotropic Gd ion for the anisotropic Dy, Tb in [Mn$_3$Ln] has has little/no effect upon the out-of-phase ac susceptibility ($\chi''$) measurements (Fig. S11). Indeed, if anything the tails of the same frequency $\chi''$ component have shifted to lower temperatures, albeit with a larger magnitude. This trend continues to the [Mn$_2$Ln$_2$] family members where the Ln = Tb species (3Tb) shows a much diminished $\chi''$ signal versus [Mn$_3$Tb] and the Ln = Dy species (3Dy) shows no out-of-phase component at all (Fig. S11). It therefore appears that, at least in this family of complexes, it is the exchange between the metal ions that is the pre-requisite for observing SMM behaviour at higher temperatures; indeed the particular topology of the [Mn$_3$Ln$_2$] family sees a move away from an exchange-coupled molecule towards a paramagnet with increasing Ln encapsulation. Unravelling the complexities of the magnetisation relaxation will however require detailed theoretical calculations, and these will follow in a subsequent full paper.
Figure 4. Energy spectra of 1-3 at zero magnetic field, for the isotropic part of spin-Hamiltonian (1), with the determined best-fit parameters, as described in the text.

Conclusions

In summary we have shown that it is possible to systematically replace the central MnII ions in a series of C[4]-supported butterflies with LnIII ions while maintaining the structural integrity of the cluster as a whole. The persistence of the [TMnIII(TBC[4])(OH)(solvent)] metallogand suggests that this approach may apply to other C[n]-supported clusters, and that these magnetic building blocks can be employed to encapsulate a wide range of different “guests” within robust “hosts”. The systematic structural transformations in the C[4]-supported butterfly motif allows for a unique study into the prevailing magnetic properties. The replacement of MnII for GdIII allows for the examination of the transferability of spin-Hamiltonian parameters within the family as well as permitting their reliable determination. The introduction of the 4f ions at the central body positions of the cluster results in weaker intramolecular magnetic exchange, an increase in the number of low-lying excited states, and an increase in magnetisation relaxation, highlighting the importance of exchange over single-ion anisotropy for the observation of SMM behaviour in this family of complexes.

Experimental Section

TBC[4] was prepared according to literature procedure. All other chemicals were purchased from commercial sources and used as supplied. Synthesis of 2: Mn(NO3)2·4H2O (0.151 g, 0.6 mmol), Gd(NO3)3·6H2O (0.271 g, 0.6 mmol), TBC[4] (0.195 g, 0.3 mmol) and NEt3 (0.35 mL, 2.4 mmol) were dissolved in a mixture of dmso (10 mL) and EtOH (10 mL) and stirred for two hours. Crystals suitable for single crystal X-ray diffraction studies were obtained in reasonable yield (25%) after filtration and diffusion of acetonitrile into the mother liquor. Elemental analysis (%) calculated for C108H163.75N1.75O22.25S5.25GdMn3: C 55.60, H 7.07, N 1.07; Found: C 55.98, H 6.95, N 0.87. The Y, Tb, Dy and Ho analogues were prepared under the same conditions (Supporting Information). Crystal data for 2 (CCDC 1030021): C108H163.75N1.75O22.25S5.25GdMn3, M = 2333.04, Purple Block, 0.31 × 0.26 × 0.22 mm3, triclinic, space group P-bar 1 (No. 2), a = 12.80(2), b = 19.21(3), c = 25.39(4) Å, α = 105.72(4), β = 104.12(3), γ = 94.78(3)°, V = 5752(15) Å3, Z = 2, Bruker X8 Apex II CCD Diffractometer, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, 2θmax = 52.7º, 87234 reflections collected, 23356 unique (Rint = 0.0793). Final Goof = 1.167, R1 = 0.1194, wR2 = 0.2650, R indices based on 18290 reflections with I >2sigma(I) (refinement on F2).

Synthesis of 3: MnCl2·4H2O (0.119 g, 0.6 mmol), GdCl3·6H2O (0.223 g, 0.6 mmol), TBC[4] (0.195 g, 0.3 mmol) and NEt3 (0.35 mL, 2.4 mmol) were dissolved in a mixture of dmso (10 mL) and MeOH (10 mL) and stirred for two hours. Crystals suitable for single crystal X-ray diffraction studies were obtained in reasonable yield (25%) after filtration and diffusion of 2-propanol into the mother liquor. Elemental analysis (%) calculated for C124H210Cl2O26S8Gd2Mn2: C 51.91, H 7.38; Found: C 51.67, H 7.13. The Y, Tb, Dy and Ho analogues were prepared under the same conditions (Supporting Information). Crystal data for 3 (CCDC 1030022): C124H210Cl2O26S8Gd2Mn2, M = 2868.68, Purple Block, 0.40 × 0.30 × 0.25 mm3, triclinic, space-group P-1 (No. 2), a = 12.5389(5), b = 16.5451(6), c = 18.9438(6) Å, α = 105.046(2), β = 91.395(2), γ = 112.075(2)°, V = 3484.3(2) Å3, Z = 1, Bruker X8 Apex II CCD Diffractometer, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, 20max = 51.4°, 52040 reflections collected, 13134 unique (Rint = 0.0440). Final Goof = 1.039, R1 = 0.0455, wR2 = 0.1095, R indices based on 11456 reflections with I >2sigma(I) (refinement on F2).

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**Keywords:** Calixarenes • Clusters • Magnetism • SMMs • Coordination Chemistry


[16] a) It should be noted that this structural search is unique to Mn and that there are other 3d-4f butterflies in the literature. For example see: M. Murugesu, A. Mishra, W. Wernsdorfer, K. A. Abboud, G. Christou, *Polyhedron*, 2006, 25, 613.


The central Mn$^{II}$ ions in a series of calix[4]arene-stabilised butterflies can be sequentially replaced with Ln$^{III}$ ions, systematically transforming the magnetic properties. This study highlights a) the importance of exchange over single-ion anisotropy for the observation of SMM behaviour in this family of complexes and b) the potential of using metalloligands to encapsulate a range of different ‘guests’ within structurally robust ‘hosts’.

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