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Linked Supramolecular Building Blocks for Enhanced Cluster Formation

Ross McLellan, Maria A. Palacios, Christine M. Beavers, Simon J. Teat, Stergios Piligkos, Euan K. Brechin, and Scott J. Dalgarno
Abstract: Methylene-bridged calix[4]arenes have emerged as extremely versatile ligand supports in the formation of new polymeric clusters possessing fascinating magnetic properties. Metal ion binding rules established for this building block allow one to partially rationalise the complex assembly process. The ability to covalently link calix[4]arenes at the methylene bridge provides significantly improved control over the introduction of different metal centres to resulting cluster motifs. Clusters assembled from bis-calix[4]arenes and transition metal ions or 3d-4f combinations display characteristic features of the analogous calix[4]arene supported clusters, thereby demonstrating an enhanced and rational approach towards the targeted synthesis of complex and challenging structures.

Introduction

Many strategies have been employed in the synthesis of polymeric clusters of paramagnetic metal ions. These range from serendipitous assembly through to rational design, the latter of which naturally relies on targeted ligand composition. The ultimate goal is the same in all cases, that being the isolation of molecules that are of interest to chemists, physicists and theoreticians due to the prevailing magnetic properties. Predicting the assembly of such clusters from multi-component systems, especially from a viewpoint of tailoring their magnetic properties, represents a significant challenge to the synthetic coordination chemist.\[1,2\] p-tBu-calix[4]arene (TBC[4]) has emerged as a highly versatile building block for the construction of polynuclear transition metal (TM), lanthanide metal (LnM) and 3d-4f clusters.\[3–10\] Its polyphenolic character allows it to: 1) bind, and 2) bridge to metal centres within clusters. We have used TBC[4] to form a library of clusters in which TM/LnM-TBC[4] moieties act as capping vertices (Figure 1A–D). Our first significant development was isolation of a family of MnIII,MnII,(TBC[4])2, single-molecule magnets (SMMs; Figure 1A).\[4,5\] The central polymeric core is an unusual butterfly in that the oxidation states are reversed relative to those typically observed with other ligands.\[11\] This occurs because the Jahn–Teller distorted, axially elongated MnIII ions are preferentially bound in the TBC[4] pocket; TBC[4] provides a stable coordination environment for a metal ion that can accommodate four short equatorial and two long axial bonds. The TBC[4] O atoms bridge to the centrally located MnIII ions and the structure can be viewed rather simply as two [MnIII(TBC[4])(OH)(DMF)] metalloligands encapsulating two “naked” MnIII ions, the remaining coordination sites of which are filled with solvent. The concept that two or more MnIII metalloids can encapsulate other metal ions in a centrally located pocket therefore suggests that a variety of homo- and heterometallic cages with similar structures should be isobaric. Indeed we recently found it possible to tailor the butterfly composition so as to systematically incorporate LnMIII ions in place of one or both MnIII ions within MnIII,LnMII,TBC[4], clusters (where \(x = 4/y = 0\), \(x = 3/y = 1\) and \(x = 2/y = 2\), thereby representing unprecedented structural control.\[12\] Analogous reactions with LnMIII ions in the absence of TMIII or TMIV ions affords LnMIII,TBC[4], octahedra (Figure 1A).\[9\] In addition we have synthesised a series of square-within-square 3d-4f clusters (MnIII,LnMIII,TBC[4]n, LnM = Gd, Tb or Dy) in which four [MnIII(TBC[4])(OH)(DMF)] metalloids encapsulate four “naked” LnIII ions. These behave as SMMs or cryogenic magnetic refrigerants depending on the LnM employed (Figure 1B).\[6,7\] Finally, treatment of TBC[4] with CuII salts affords enneanuclear clusters that display versatile anion binding capabilities.\[10\] These display an interesting structural departure in that the polyphenolic pocket binds CuII ions to form moieties that cap a CuII trigonal prism (Figure 1C). From these key developments we have established metal ion binding rules for TBC[4]. We have found that under ambient conditions TBC[4]: 1) preferentially binds MnIII ions, 2) will bind TMIV ions (e.g., CuII and CoII) in the absence of TMIII ions (e.g., MnIII), and 3) will bind LnMIII ions in the absence of TMIII or TMIV ions.

A range of molecules comprising TBC[4]s modified at the methylene bridge were recently reported in the literature, including linked C[4]s.\[13\] This presented an opportunity to build on the TBC[4] binding rules by having two metal ion complexation sites within bis-TBC[4] (Figure 1E). We therefore predicted that, upon structural rearrangement of the ligand, it would be possible to construct: 1) MnIII/MnII clusters comprising more than two [MnIII,TBC[4]]n− moieties, 2) LnMII clusters comprising more than two [LnMIII,TBC[4]]n− moieties (in the absence of TMIII/TMIV ions), 3) 3d-4f clusters containing more than two [MnIII,TBC[4]]n− moieties and LnMIII ions from Mn/LnM combinations, and 4) polynuclear CuII clusters containing more than two [CuII-TBC[4]]3− moieties (in the absence of other TMIII/TMIV ions). In the first of our experiments we have achieved
to proceed in the solution phase with very low accompanying energy barriers.\textsuperscript{14} Extension of this to \(\text{H}_8\text{L1}\) allows for the possibility that two sets of TBC[4] phenolic oxygen atoms may, upon rotation/inversion, orient such that they are directed toward a central point. Furthermore, the proximity of two phenolic oxygen atoms from each TBC[4] fragment would present additional binding sites for metal ions. In particular we anticipated that \(\text{H}_8\text{L1}\) would allow us to controllably introduce multiple metal centres of predetermined oxidation states (e.g., two [Mn\textsuperscript{III}-TBC[4]]\textsuperscript{4\textsuperscript{-}} moieties) in order to enhance the formation of new polynuclear metal clusters.

Results and Discussion

Reaction of \(\text{H}_8\text{L1}\) with manganese(II) chloride hydrate in a DMF/MeOH mixture and in the presence of base afforded single crystals of [Mn\textsuperscript{III}\textsubscript{4}Mn\textsuperscript{II}\textsubscript{4} (L1)\textsubscript{2}(\text{m}_3\text{-OH})\textsubscript{2}(\text{m}_3\text{-OH})(\text{m}_3\text{-Cl})(\text{H}_2\text{O})(\text{MeOH})(\text{dmf})\textsubscript{4}]·2\text{H}_2\text{O}·12\text{MeCN} (1), following slow diffusion with acetonitrile (Figure 2).\textsuperscript{15} The isolated complex contains a mixed valence Mn\textsuperscript{III}\textsubscript{4}Mn\textsuperscript{II}\textsubscript{4} cluster that is strikingly similar to the archetypal Mn\textsuperscript{III}\textsubscript{2}Mn\textsuperscript{II}\textsubscript{2} butterfly motif isolated with TBC[4].\textsuperscript{4, 5} Both L1 ligands in 1 are arranged such that one TBC[4] fragment has undergone inversion, presumably as a consequence of metal ion coordination. In this conformation L1 is ideally suited to controllably insert two Mn\textsuperscript{III} ions into a cluster. Furthermore, additional binding sites between the TBC[4] fragments in each L1 are occupied by Mn\textsuperscript{II} ions. The structure of 1 is best described as two L1-supported distorted Mn\textsuperscript{III}\textsubscript{2}Mn\textsuperscript{II}\textsubscript{2} butterflies, or alternatively as two Mn\textsuperscript{III}-TBC[4] metalloligands encapsulating two “naked” Mn\textsuperscript{II} ions. The metal ions are linked together by bridging phenolates, hydroxide and chloride (or formate generated by in situ hydrolysis of dmf). The metal core and coordination environment relating to each “Mn 4” (Mn\textsubscript{1–4} cf. Mn\textsubscript{5–8}) is essentially the same, and so only one half of the metal cluster will be described in detail. Mn\textsubscript{1} is centrally bound to four fully deprotonated phenolic oxygen atoms O1–O4 (Mn–O range 1.865(3)–1.956(3) \AA) of one TBC[4] moiety. As three of these four objectives, and the resulting clusters display predicted structural characteristics within a series of spectacular new motifs, all of which demonstrate a significant step towards the targeted assembly of polymeric species. Bis-TBC[4] (H\textsubscript{8}L1) was synthesised according to literature procedure,\textsuperscript{13} and upon crystallisation was found to adopt an up-down twisted arrangement (Figure 1 E). The TBC[4] cavities are stabilised by lower-rim H bonding, point in alternate directions, and neighbouring molecules assemble to form an antiparallel bilayer (Figure S1 in the Supporting Information) reminiscent of that observed for TBC[4]. The conformational versatility of calixarenes is generally well understood; the CH\textsubscript{2} bridges between phenyl rings impart flexibility that allows ring inversion.
predicted the square pyramidal Mn1 is in the third oxidation state and its coordination is completed by bonding to a μ-hydroxide (Mn1–O21 2.126(3) Å), which is further bonded to Mn3 and Mn4 (2.152(3) and 2.155(3) Å, respectively), both of which are in the second oxidation state; Mn3 lies in the binding pocket generated by inversion. In addition to O21, Mn3 is bonded to dmf (Mn3–O18 2.121(3) Å) and three μ-phenoxide oxygen atoms (Mn3–O4 2.266(3) Å and Mn3–O5 2.175(3) Å). The remaining two coordination sites display extensive disorder. The first component describes a distorted octahedral metal ion bonded to a half occupancy μ-Cl (Mn3–Cl1 2.800(5) Å) that also connects to Mn7, and a MeOH/H2O ligand that have each quarter occupancy (Mn3–O24 2.196(5) Å).[16] Mn4 occupies the remaining binding cavity within L1. It is square pyramidal and is coordinated to, alongside O21, one dmf ligand (Mn4–O18 2.121(3) Å) and three μ-phenoxide oxygen atoms (Mn4–O1 2.208(2) Å, Mn4–O8 2.102(3) Å and Mn4–O15 2.129(3) Å). Mn2 is centrally bound to all four fully deprotonated phenolic oxygen atoms (O5–O8) of the second TBC[4] fragment of L1 (Mn–O range 1.902(3)–1.967(3) Å). It is also in the third oxidation state and possesses square pyramidal geometry. Mn2 is further bonded to a μ-hydroxide (Mn2–O23 2.067(3) Å), which bridges to the other similar “Mn4 cluster” within 1 (containing Mn5–Mn8).

Examination of the extended structure reveals that molecules of 1 pack in a complex fashion with adjacent clusters being well isolated (closest Mn–Mn distance ca. 13.1 Å). Along one direction, molecules assemble into an infinite chain such that two molecules of 1 lie perpendicular to, and sandwiched between, two adjacent molecules (Figure S2A in the Supporting Information). Viewing this arrangement from a perpendicular direction reveals that the four molecules assemble around a central solvent-filled channel (Figure S2B in the Supporting Information). Further packing reveals the formation of a tube-like structure (Figure S2C). While Mnα clusters are not rare (a Cambridge Structural Database [CSD] search reveals about 65 entries) it is clear that the topology of the metal core in 1 is novel and a consequence of the L1 ligand.

Treatment of H4L1 with manganese(II) chloride and gadolinium(III) chloride in a DMF/MeOH mixture in the presence of base afforded single crystals of formula [Mn10−2Mo3+Mnα8−2(L1−8H)4]2[μ3−OH]2(MeOH)2(dmfn)2(Et2O)0.5(dmfn) (2) upon slow diffusion with diethyl ether (Figure 3). Structural analysis reveals, as predicted, that each TBC[4] fragment contains an Mn10−2 ion. As in 1, the L1 ligands have undergone inversion, leading once more to additional binding pockets for metal ions. The metal core of 2 bears a remarkable similarity to 1, the main difference being replacement of one Mn10−2 for one GdIII in the binding site located between the two TBC[4] cavities of each L1. The central core is best described as a central Mn10−2-GdIII, butterfly motif that is edge fused (sharing one Mn10−2 ion and one GdIII ion) to two symmetry equivalent (s.e.) peripheral Mn10−2-GdIII butterflies; Mn10−2-TBC[4] moieties are again found to encapsulate “naked” Mn10−2 and GdIII ions. The central butterfly contains two s.e. distorted octahedral Mn10−2 ions (Mn3 and Mn3′) that each reside within a TBC[4] pocket. The coordination sphere of Mn3 consists of four phenolic oxygen atoms (one terminal and three bridging, with Mn3–O ranging from 1.872(4)–1.992(4) Å), a ligated dmf (Mn3–O11 2.224 Å) and a μ3-hydroxide (Mn3–O9 2.162(4) Å). The O(dmf)–Mn3–O9(μ3–OH−) vector defines the Jahn–Teller axes with significant deviation from linearity (164.7(2°)). The central GdIII ions (Gd1 and s.e.) are located in the binding sites situated between the two TBC[4] cavities of each L1 and are found to be seven coordinate (distorted pentagonal bipyramidal geometries). Each is bonded to the aforementioned μ3-hydroxide, O9, its s.e. (Gd1–O9 2.381(4) Å...
and Gd1–O9’ 2.362(4) Å, respectively), and to a second µ₃-hydroxide, O10 (Gd1–O10, 2.328(4) Å). These are also coordinated to a ligated dmf and three µ-phenolic oxygen atoms (Gd1–O1 2.425(4) Å, Gd1–O8 2.298(4) Å and Gd1–O7’ 2.344(4) Å). Mn2 also resides in the cavity generated by the two TBC[4] fragments and has a distorted octahedral geometry. It is coordinated to a chloride ion (Mn2–Cl1 2.470(2) Å), two µ-phenolic oxygen atoms (Mn2–O4 and Mn2–O5, 2.342(4) and 2.212(4) Å, respectively), a µ₃-hydroxide (Mn2–O10 2.165(4) Å), ligated dmf (Mn2–O14 2.096(4) Å) and ligated MeOH (Mn2–O15 2.271(4) Å). Mn1 (and s.e.) is coordinated centrally in the binding cavity of one TBC[4] fragment of L1 and has Mn1-phenolic oxygen lengths in the range 1.883(4)–1.976(4) Å. Two of these oxygen atoms (O1 and O4) bridge to Mn2 and Gd1, vide supra. Along the Jahn–Teller axis, Mn1 is coordinated to a µ₃-hydroxide (Mn1–O10 2.195(4) Å) and a terminally bound dmf (Mn1–O12 2.243(4) Å) in the TBC[4] cavity. Adjacent clusters of 2 pack in a simple head-to-head zig–zag fashion (Figure S3 in the Supporting Information), each cluster being well isolated with closest distances of about 14.0 Å. A CSD search was performed to assess the structural novelty of 2. Three entries were returned for Mn₆Gd₂ species, each containing a different topology from 2. A second more general search for Mn₆Ln₂ was performed and this returned only eight entries, again all with different topologies.

Treatment of copper(II) nitrate hydrate with H₈L1 in a basic medium of DMF/MeOH afforded [Cu²⁺(L1)₃(NO₃)₃(μ-OH)₈(dmf)₇·(OH)(MeCN)₁₄] (3) following diffusion of acetonitrile (Figure 4). Structure analysis reveals a Cu³⁺ cluster supported by two inverted L1 ligands. The TBC[4] pockets and additional binding sites are all occupied by Cu³⁺ ions (Figure 4 A). The two Cu⁻L₁ moieties are connected by four additional Cu³⁺ ions (Figure 4 B), giving a polymetallic core that conforms to a tetracapped diamond (or tetracapped square prism). Each face is thus capped by a TBC[4]-Cu³⁺ moiety, with the overall framework bearing obvious similarity to the tricapped trigonal prismatic Cu⁴⁺ clusters isolated from analogous reactions with TBC[4] (Figure 1 C). That is, the latter describes three Cu²⁺TBC[4] metalloligands encapsulating a trigonal prism, and the former describes four Cu³⁺TBC[4] metalloligands encapsulating a square prism. The remaining Cu²⁺ ion in 3 resides in the centre of the prism and is disordered over several positions. The four capping Cu³⁺ ions are in distorted square planar geometries and bond to all four phenolic oxygen atoms of each TBC[4] subunit (Cu–O range 1.926(5)–1.966(5) Å). Four distorted square planar Cu³⁺ ions connect the two L1 ligands in 3 via O–Cu–O bridges (Cu–O range 1.914(5)–1.976(14) Å). Furthermore, each pair of bridging Cu³⁺ ions is linked by a µ-OH (Cu–O range 1.914(5)–1.932(4) Å). Coordination is completed by bonding to either dmf or a nitrate ligand. The four Cu³⁺ ions that reside in the binding sites between each TBC[4] fragment of L1 are either distorted trigonal bipyramidal or distorted tetrahedral, a fact largely dependent on the location of the final extensively disordered Cu³⁺ ion. These five Cu³⁺ ions are interconnected by a combination of five µ-OH ligands giving a caticonic cluster.

The TBC[4],Cu⁴⁺ cluster has been found to be a versatile anion binding material, with the core adapting such that three µ-hydroxides can be replaced by a µ₃-carbonate, for example. The outer Cu²⁺,₂ skeleton of 3 may thus potentially bind a range of different cations (organic or inorganic in nature), and this will be explored in detail in future studies. Analysis of the extended structure reveals that the assembly of 3 is best described as offset linear chains (Figure S4 in the Supporting Information).
Information). As expected, the metallic core in 3 is well isolated from adjacent clusters with a closest Cu···Cu distance of about 13 Å. A CSD search was performed to determine the novelty of the metallic skeleton in 3. This returned one entry in which a Cu\textsubscript{13} cluster conforms to a pinwheel-like structure that is markedly different to that found in 3.[17]

Direct current (d.c.) magnetic susceptibility studies were performed on polycrystalline samples of 1–3 in the temperature range 5–300 K in an applied magnetic field of 0.1 T. The results are shown in Figure 5 in the form of $\chi_M T$ products, where $\chi = M/B$, $M$ is the magnetisation, $B$ the applied magnetic field, and $T$ the temperature.

At 300 K, the $\chi_M T$ value of 28.0 cm\textsuperscript{3} mol\textsuperscript{-1} K for 1 is lower than the value of 29.5 cm\textsuperscript{3} mol\textsuperscript{-1} K, expected for spin-only contributions to the magnetism, assuming $g = 2.0$ for both Mn\textsuperscript{II} and Mn\textsuperscript{III}, $g$ being the isotropic $g$ value. On lowering the temperature, the $\chi_M T$ product remains essentially constant down to a temperature of approximately 150 K where it begins to decrease rapidly to reach a minimum value of 10.8 cm\textsuperscript{3} mol\textsuperscript{-1} K at 5 K. The spin-Hamiltonian matrix of 1 is a square matrix of dimension 810,000 and cannot be diagonalised by standard methods.

Figure 4. Views of the single-crystal X-ray structure of the cation in 3 showing the polymetallic core. A) Crown-like arrangement of outer twelve Cu\textsuperscript{II} centres showing bridging hydroxides on the interior. B) Metallic skeleton of the cation in 3 with the capping TBC\textsubscript{4}-Cu\textsuperscript{II} moieties drawn as large spheres. H atoms, OH/NO\textsubscript{3} anions, ligated and non-coordinating solvent are omitted.

Figure 5. Experimental and best-fit $\chi_M T$ products of 1–3 in a magnetic field of 0.1 T in the temperature range 5–300 K, and low-temperature magnetisation measurements on 3 in the temperature range 2–7 K in applied magnetic fields of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 T. The inserts of the $\chi_M T$ product plots represent the pair-connectivity of the various isotropic exchange interactions taken into account in the spin-Hamiltonian models for 1–3 for each metallic skeleton.
techniques. Thus, to model the $\chi_{MT}$ product, we have employed home-written software (ITO-MAGFIT)[14] that makes use of irreducible tensor operator algebra[15] to block-diagonalise the spin-Hamiltonian matrix. ITO-MAGFIT is a magnetisation fitting program that uses the Levenberg–Marquardt algorithm.[20]

We used the general form of the isotropic spin-Hamiltonian of Equation (1) to model the $\chi_{MT}$ product:

$$\hat{H} = \mu_B \sum_i g_i \hat{S}_i \cdot \hat{H} - 2 \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

(1)

where $\mu_B$ is the Bohr magneton, the index $i$ runs through all constitutive single-ion centres, $g$ is the $g$ matrix of the $i$th single-ion, here assumed to be $g = 2.0$ for simplicity, $\hat{S}$ is a single-ion spin operator, and $J$ is the isotropic exchange parameter between a pair of metal centres. To avoid parameterisation we have assumed that all Mn II–MnII, all Mn II–MnIII and MnIII–Mn III isotropic exchange parameters are the same. This results in three independent fit parameters to account for the pairwise isotropic exchange interaction terms: $J_{1–2}, J_{1–3}, J_{2–3}, J_{2–4}, J_{3–4}, J_{4–5}, J_{5–6}, J_{6–7}, J_{7–8}$ between MnII and MnII centres (hereafter referred to as $J_{MnII-MnII}$); $J_{2–3}$ and $J_{6–7}$ between MnII centres ($J_{MnII-MnII}$); and $J_{4–5}$ between MnIII centres ($J_{MnIII-MnIII}$). These pairwise isotropic exchange parameters are schematically represented in the insets of Figure 5. Under these conditions, the best-fit parameters for $H$ are: $J_{MnII-MnII} = +0.92 \text{ cm}^{-1}$, $J_{MnII-MnII} = -4.48 \text{ cm}^{-1}$ and $J_{MnII-MnII} = -1.52 \text{ cm}^{-1}$. The best-fit curve is shown in Figure 5. These values are in good agreement with the parameters previously determined for molecules with the exchange between the CuII ions around the peripheral Cu 12 cluster construction (Figure 1). The appropriate combination of antisymmetric interaction terms, often used for the interpretation of the magnetic properties of CuII-containing complexes,[22] since these proved to be unnecessary. Thus, for the interpretation of the magnetic properties of 3 we included three free parameters in spin-Hamiltonian (Equation (1)) (Figure 5): $J_{1–2}, J_{1–3}, J_{1–11}$ are used to take into account the exchange between CuII centres bridged by hydroxides ($J_1$; the vertices of the square prism); $J_{1–2}, J_{1–3}, J_{11–11}, J_{1–12}, J_{3–13}, J_{4–13}, J_{5–13}, J_{6–13}, J_{7–13}, J_{8–13}, J_{10–13}, J_{12–13}, J_{13–13}, J_{14–13}, J_{15–13}$, are used to take into account the exchange between the CuII ions around the peripheral CuII “wheel” ($J_2$), and finally $J_{1–12}, J_{3–13}, J_{11–13}, J_{12–13}, J_{13–13}, J_{14–13}$, are used to take into account the exchange between the central CuII ion and all of its nearest neighbours ($J_3$). The best-fit parameters for 3 are: $J_1 = -84.14 \text{ cm}^{-1}$, $J_2 = -65.97 \text{ cm}^{-1}$, $J_3 = -22.69 \text{ cm}^{-1}$. With these parameters, the ground spin-state of 3 is a quadruply degenerate $S = 1/2$ state, with the first excited state being a doubly degenerate $S = 1/2$ state lying approximately 5.2 cm$^{-1}$ higher in energy. The rest of the energy spectrum of 3 also presents a high degree of degeneracy (Figure 6), suggesting a particularly exceptional case of spin-frustration.[21,24]

**Conclusions**

To conclude, three new cluster types with novel and fascinating topologies have been constructed by enhanced ligand design. All three complexes contain metal-binding properties that are entirely consistent with complexes of TBC[4], which itself can be regarded as a versatile ligand for polymetallic cluster construction (Figure 1). The appropriate combination of two (or more) conjoined ligands is an important step towards

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**References**


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enhanced control over topology, nuclearity and properties of polymeric clusters with these building blocks. Indeed the magnetic exchange between the constituent metal ions in polymetallic clusters with these building blocks. The results of which will be reported in a future communication on this topic. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Experimental Section**

Bis-TBC[4] (H₂,L₁) was synthesised according to literature procedure. Crystal data for bisTBC[4](CHCl₃)₄: C₆₀H₅₇Cl₆O₄, Mᵣ = 886.62, colourless block, 0.25 × 0.25 × 0.20 mm³, triclinic, space group P1 (No. 2), a = 11.625(2), b = 13.989(2), c = 16.333(3) Å, α = 99.775(7), β = 103.876(7), γ = 114.203(7)°, V = 2241.7(7) Å³, Z = 2, Bruker X8 Apex II CCD diffractometer, Mo Kα radiation, λ = 0.71073 Å, T = 100(2) K, 2Θmax = 48.8°, 23610 reflections collected, 7331 unique (Rint = 0.0594). Final Goof = 1.027, R1 = 0.0764, wR2 = 0.1995, R indices based on 4206 reflections with I > 2σ(I) (refinement on F²).

**Figure 6.** Energy spectrum of 3 determined as described in the main text. Top: full energy spectrum. Bottom: low-lying energy spectrum, with labels denoting the degeneracy of the states.

Synthesis of [Mnᵢii,Mnᵢi(L₁)₂(μ₂-OH)](μ₂-OH)(μ₂-Cl)(H₂O)ₐ₃ (MeOH)ₐ₃(μ₂-HCO₂)(dmf)ₐ₁₂(H₂O)₂(MeCN)₁₂ (1)

H₂,L₁ (200 mg, 0.172 mmol) and MnCl₂·4H₂O (68 mg, 0.344 mmol) were suspended in a 1:1 mixture of DMF/MeOH (24 mL). NEt₃ (0.4 mL) was added and the resulting purple solution was stirred for 90 min and then filtered. The mother liquor was allowed to diffuse slowly with acetonitrile vapour, affording a crop of crystals from which a crystal suitable for X-ray diffraction studies was obtained. Yield (101 mg, 30%); elemental analysis (%) calcd for 1, C₇₃H₇₇N₇O₅Cl₂Mn₂₄: C 64.88, H 7.09, N 5.68; found: C 65.17, H 7.25, N 5.57. Crystal data for 1: C₇₃H₇₇N₇O₅Cl₂Mn₂₄, Mᵣ = 9451.01, dark green block, 0.32 × 0.30 × 0.23 mm³, monoclinic, space group P2₁/c (No. 14), a = 16.731(3), β = 30.607(6), c = 21.746(4) Å, β = 101.89(3)°, V = 42739(3) Å³, Z = 2. Bruker APEX II CCD diffractometer, synchrotron radiation, λ = 0.77490 Å, T = 100(2) K, 2Θmax = 45.9°, 302,992 reflections collected, 39,354 unique (Rint = 0.0683). Final Goof = 1.700, R1 = 0.0788, wR2 = 0.2362, R indices based on 30,436 reflections with I > 2σ(I) (refinement on F²).

Synthesis of [Mnᵢii,Mnᵢi,Gdᵢiv(L₁–BH₂)(Cl)₂(μ₂-OH)₂(MeOH)₂(dmff)₁₂(Et₂O)₁₂(dmf)₁₂ (2)

H₂,L₁ (200 mg, 0.172 mmol), MnCl₂·4H₂O (68 mg, 0.344 mmol) and GdCl₃·6H₂O (64 mg, 0.172 mmol) were stirred in a solvent mixture of DMF/MeOH (12 mL:2 mL). NEt₃ (0.4 mL) was added and the reaction was stirred for 90 min. After filtration, a crop of dark green block crystals, suitable for X-ray diffraction studies, were grown by vapour diffusion of the mother liquor with diethyl ether. Yield (81 mg, 21%); elemental analysis (%) calcd for 2, C₁₄₃H₁₄₈Nd₄Cl₂Gd₂Mn₂₄N₂₄O₆ₐ₄: C 60.71, H 7.45, N 2.83; found: C 60.30, H 7.14, N 2.95. Crystal data for 2: C₁₄₃H₁₄₈Nd₄Cl₂Gd₂Mn₂₄N₂₄O₆ₐ₄, Mᵣ = 4451.01, dark green block, 0.10 × 0.10 × 0.02 mm³, triclinic, space group P1 (No. 2), σ = 16.731(3), b = 30.607(6), c = 21.746(4) Å, β = 101.89(3)°, V = 42739(3) Å³, Z = 2. Bruker X8 Apex II CCD diffractometer, Mo Kα radiation, λ = 0.71073 Å, T = 100(2) K, 2Θmax = 55.9°, 85,629 reflections collected, 22,772 unique (Rint = 0.0697). Final Goof = 1.122, R1 = 0.0656, wR2 = 0.1398, R indices based on 15,709 reflections with I > 2σ(I) (refinement on F²).

Synthesis of [Cuᵢii(L₁)(NO₃)₂(μ₂-OH)ₐ₁₂(Oh)(MeCN)₁₂ (3)

H₂,L₁ (200 mg, 0.172 mmol) and Cu(NO₃)₂·3H₂O (108 mg, 27%); elemental analysis (%) calcd for 3, C₇₃H₇₇N₇O₅Cu₂: C 57.46, H 6.52, N 6.55; found: C 57.16, H 6.60, N 6.81. Crystal data for 3: C₇₃H₇₇N₇O₅Cu₂M₄ = 4605.08, brown needle, 0.10 × 0.10 × 0.02 mm³, triclinic, space group P1 (No. 2), a = 17.7475(6), b = 18.0586(6), c = 20.5598(7) Å, β = 90.487(2), γ = 111.201(2), V = 5661.1(3) Å³, Z = 1, Bruker APEX II CCD diffractometer, synchrotron radiation, λ = 0.77490 Å, T = 100(2) K, 2Θmax = 67.4°, 88,572 reflections collected, 34,420 unique (Rint = 0.0482). Final Goof = 1.028, R1 = 0.1425, wR2 = 0.3827, R indices based on 26,828 reflections with I > 2σ(I) (refinement on F²).
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