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Topological Self-Assembly of Highly-Symmetric Lanthanide Clusters: A Magnetic Study of Exchange-Coupling “Fingerprints” in Giant Gadolinium(III) Cages

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KEYWORDS: High-symmetry • Antiferromagnetic • Heisenberg model • Gadolinium • Polyhedra

ABSTRACT: The creation of a perfect hollow nanoscopic sphere of metal centres is clearly an unrealisable synthetic challenge. It is however an inspirational challenge, from the viewpoint of chemical architecture and also as finite molecular species may provide unique microscopic insight into the origin and onset of phenomena such as topological spin-frustration effects found in infinite 2D and 3D systems. Herein, we report a series of high symmetry gadolinium(III) (S = 7/2) polyhedra, Gd20, Gd32, Gd50, and Gd60, to test an approach based on assembling polymetallic fragments that contain different polygons.

In the majority of cases an Archimedean solid, where all faces are identical (Figure 1),12 Therefore we reason that to construct a metal polyhedron that approaches a sphere in structure, a mixture of different polygons should be used.3 This may initially appear counter-intuitive. In some ways it builds from previous topological analysis which showed that a “magic” pentagon {Mo}Mo2 is critical in constructing highly-symmetric spherical polyoxometallates (POMs).4 implicit in that analysis is that some of the polygons linking the magic pentagons have a different number of edges.

Highly symmetric arrangements of paramagnetic centres are expected to show exotic spin frustration effects if they are coupled antiferromagnetically as it is impossible to align all spins anti-parallel to all nearest neighbours.5 This can lead to unusual fundamental new physics such as metamagnetic phase transitions and unexpected hysteresis effects.6 However, a necessary ingredient in order to find such effects experimentally requires spin centres that behave like pure spins, i.e. any significant single ion anisotropy is absent.

Here we build high symmetry gadolinium(III) cages (Table S1), using a topological knowledge of lanthanide (Ln) fragments, such as the (Ln(μ-OH)) triangle, (Ln(μ-OH)2) square, (Ln(μ2-OH))3 tetrahedron, (Ln(μ5-CO3)) pentagon and (Ln6(μ6-CO3)) hexagon (Figure S1). Gadolinium(III) was chosen as its spin moment is very large (S = 7/2) and its orbital moment is zero and hence it is ex-
pected to behave like a classical spin centre. This allows us to model such systems classically since a quantum treatment is impossible due to the large number of interacting magnetic moments.

RESULTS

Synthetic strategy and overview of structural motifs. Our synthetic strategy involves using simple anions as weak templates in the presence of other multidentate ligands; on occasion trapping a polymetallic intermediate allows us to build pseudo-spherical cages that are not otherwise accessible.

For example: a \( \text{Gd}_{60} \) cage of formula \( [\text{Gd}_{60}(\text{CO}_3)_8(\text{OH})_{28}(\text{dmp})_{10}(\text{H}_2\text{O})_{10})(\text{NO}_3)_{32} \) can be made directly from reaction of hydrated gadolinium nitrate with 2,2-dimethylol propionic acid (Hdmp) at 130 °C in mixed solvents (CH\(_3\)CN/CH\(_3\)OH/H\(_2\)O) under solvothermal conditions (see Supporting information for details). The aqueous solution involved contains a large quantity of base and is exposed to air prior to reaction, which leads to formation of carbonate which is the simple anion that favours the formation of \( \text{Gd}_{60} \) (Figures 2, 4 and S2). A similar \( \text{Er}_{60} \) cage has been reported by Zheng et al.\(^7\)

The structure can be viewed as a truncated octahedron of Gd(III) tetrahedron units with 6.222-bridging (Harris notation\(^8\)) \( \text{CO}_3^{2}\) anions on the slightly distorted hexagonal faces. The tetrahedron of Gd(III) centres are formed by \( \mu_5- \) bridging hydroxides. The outermost Gd(III) centres are surrounded by dmp\(^-\) ligands which show two binding modes: 2.0111 and 3.1112. The Gd(III) ions are eight- or nine-coordinate and the Gd∙∙∙Gd separations in \( \text{Gd}_{60} \) range from 3.56 to 3.95 Å. This compound is clearly a stable thermodynamic product given reaction conditions.

Figure 2. The synthetic strategy of the four high-symmetry spherical Gd(III) polyhedral and two intermediates. Colour codes: Gd, dark green; C, gray; O, pink; Cl, yellow. The synthetic paths from I to VII correspond to the synthesis of \( \text{Gd}_{60}, \text{Gd}_{15}, \text{Gd}_{50}, \text{Gd}_{20}, \text{Gd}_{32}, \text{Gd}_{32}, \text{Gd}_{9} \), respectively (for details see Methods part). The direct synthesis of \( \text{Gd}_{50} \) from simple gadolinium salts is not feasible.

To divert the reaction away from \( \text{Gd}_{60} \) we add sodium chloride as a weak templating agent. Even then, if we heat directly to 130 °C solvothermally we still produce \( \text{Gd}_{60} \), however stirring at 90 °C allows us to trap an intermediate; this compound, \( [\text{Gd}_{15}(\mu_5-\text{Cl})(\text{OH})_{20}(\text{dmp})_{10}(\text{H}_2\text{O})_{10})(\text{ClO}_4)_{6}\text{Cl}_6 \), \( \text{Gd}_{15} \), contains a \( \mu_5- \)
bridging chloride at the centre of a pentagon of \{Gd\}_4 tetrahedron. The \{Gd\}_4 tetrahedra are similar to those in Gd_{60} and it is the presence of a chloride that acts as a template for a pentagon that produces this new cage (Figures 2, 4 and S3). The dmp ligands exhibit the 3.1112-mode, chelating the outmost Gd(III) centres of each \{Gd\}_4 tetrahedron. The Gd(III) ions are coordinated with 7–9 oxygen atoms and the separations between adjacent Gd(III) range from 3.61 to 3.92 Å.

The Gd_{15} cage can be isolated and then further reacted under solvothermal conditions (150 °C) to produce Gd_{50}(μ_5-Cl)_{12}(OH)_{30}(dmp)_{30}(H_2O)_{60}Cl_8 Gd_{50} (Figures 2, 3 and S4). The Gd_{50} structure can be described as resulting from twelve Gd_{15} molecules sharing edges of the \{Gd\}_4 tetrahedron. More classically, it is a Keplerate constructed from an outer pentagonal dodecahedron and an encapsulated icosidodecahedron (formed by 12 pentagons and 20 triangles) core. The icosidodecahedron is well known from the Fe_{30} Keplerate reported by Müller and co-workers, but the polyhedron in Gd_{50} containing the outer Platonic polyhedron is unprecedented. The Gd(III) ions are eight- or nine-coordinate and the Gd⋯Gd separations between the adjacent Gd(III) ions are from 3.61 to 3.93 Å. The core is covered by dmp ligands exhibiting the 3.1112 and 3.0112 fashions.

The chemistry to give Gd_{15} and Gd_{50} relies on chloride templating the formation of pentagons of \{Gd\}_4 tetrahedron. Less predictable pentagons are found when 2-chloro-6-hydroxy pyridine (Hchp) is reacted with gadolinium nitrate in basic conditions in the CH_3CN/CH_3OH mixed solvents; again producing carbonate as a co-ligand. The result is [Gd_{20}(chp)_{10}(CO_3)_{12}(NO_3)_{6}(H_2O)_6] Gd_{20}, with the metal sites lying on the vertices of a pentagonal dodecahedron (Figures 2, 3 and S5). Again, this appears to be a new isolated polyhedron for homometallic lanthanide cages; it has been found within 3d-4f cages, where the 4f-ions make a dodecahedron inside a icosidodecahedron of Ni(II) ions. It is also the last of the Platonic solids to be reported as a structural motif in a cage. All of the Gd(III) are nine-coordinate with nearest Gd⋯Gd separations ranging from 3.82 to 4.00 Å. The Gd_{20} cluster core is encapsulated by the chp ‘ligands, each adopting a 2.21-coordination mode and with its chlorine atom pointing away from the cluster cage. This pentagonal dodecahedron is far smaller than the same polyhedron found in Gd_{50} (diameter 12.3 cf. 19.5 Å, see Figure 4).

Figure 3. Structures of four spherical cluster compounds Gd_{20}, Gd_{32}, Gd_{50} and Gd_{60}, arranged from left to right by increasing nuclearity. Upper, core structures of the four clusters with main bridges and the size (diameter) of each cluster indicated below; lower, topological representation of four clusters, together with the point group and volume ratios (V_{polyhedron}/V_{circumsphere}) based on the outmost shell.
The final polyhedron we discuss is \[\text{[Gd}_{32}\text{(OH)}_{10}\text{(mda)}_{4}\text{(NO)}_{2}\text{(H}_{2}\text{O})_{2}\text{2-}(\text{CH}_{3}\text{OH})_{4}]\] (Figures 2, 4 and S7). This is a polyhedron based on two vertex-sharing square-based pyramids; \(\mu\)-hydroxides are found at the centre of each triangular face of this polyhedron while the basal distorted square contains a \(\mu\)-hydroxide. The Gd(III) ions are eight- or nine-coordinate and the Gd····Gd separations between the adjacent Gd(III) ions are from 3.59 to 3.83 Å. It is worth speculating that this structure is the nucleating point for the \text{Gd}_{32} \text{core} since it forms first and then the further hydroxide-centred triangles grow around this cage, companied with the reconstruction of the core structure. Vertex-sharing square pyramidal cores have been reported previously.\(^{12}\) In all of the six complexes, the Gd-O bond lengths locate in the range from 2.23 to 2.82 Å, which are normal in Gd(III)-hydroxide clusters.

![Figure 4. The core structures of compounds Gd15 and Gd9.](image-url)

The synthetic strategy is based on assembling polymetallic fragments which we believe form initially: fragments such as a \{Gd\_{(\mu\_2-OH)}\} triangle, \{Nd\_{(\mu\_2-OH)}\} square, \{Gd\_{(\mu\_2-OH)}\}_{4} tetrahedron (which is built from triangles), \{Gd\_{(\mu\_5-Cl)}\} pentagon and \{Gd\_{(\mu\_6-Co)}\} hexagon. Specific anionic templates such as \text{OH}^{-}, \text{Cl}^{-} and \text{CO}_3^{2-}, certain solvents and organic ligands control the distribution of such fragments. This is then followed by aggregation into larger pseudo-spherical clusters. Most of these giant cluster species require a reaction conditions with relatively high temperature and pressure provided in situ by solvothermal conditions; this suggests they are often thermodynamic products. In some cases intermediate structures such as Gds can be trapped, and the reaction re-directed towards new high symmetry species. The organic ligands involved play an important role in both the hydrolysis of hydrated gadolinium ions and then stabilise the clusters by providing protective organic shells around the four unprecedented nano-sized spherical clusters. The small inorganic ligands are far more structure directing than the larger polynucleating organic ligands, and this may again appear counter-intuitive but is connected to the flexibility of the organic ligands used here.

In terms of core topology, the four largest cages (Gd_{20}, Gd_{32}, Gd_{50} and Gd_{60}) are all closed surfaces with the Euler characteristic \(\chi = 2\) (Table S2). According to Euler’s rule the \text{Gd}_{32} core is equivalent to the smallest fullerene structure C_{20}. The \text{Gd}_{32} and the \text{Gd}_{50} cores are new in metal cage complexes.\(^{11,13}\) Interestingly, the polyhedral surface of the \text{Gd}_{32} core is close to an ideal sphere with a ratio of \(V_{polyhedron}/V_{Vesrahedron} = \sim 81\%\) which is higher than an previously reported gadolinium cage (the previous largest one is the \text{Gd}_{104} cage with \(\sim 76\%\)). For comparison, the parent fullerene, C_{60}, has a ratio of \(\sim 87\%\) with twelve pentagons and twenty hexagons.

**Magnetic studies.** The magnetic properties of six Gd(III) complexes, \text{Gd}_{9}, \text{Gd}_{15}, \text{Gd}_{20}, \text{Gd}_{32}, \text{Gd}_{50} and \text{Gd}_{60}, were studied on polycrystalline samples. In all cases the high temperature limiting value of the product \(\chi T\) (where \(\chi\) is the molar magnetic susceptibility) is in good agreement with the calculated spin-only value for the number of independent paramagnetic Gd centres present (Figure 5). For all compounds \(\chi T\) decreases with decreasing temperature, indicating the presence of weak antiferromagnetic interactions between the Gd centres but in all cases the value of \(\chi T\) is non-zero at 2 K, which is the lowest temperature measured. This indicates paramagnetic states are still populated at this temperature. Temperature-dependent measurements are shown in the supplementary material.

The magnetization (\(M\)) of all compounds was measured versus external magnetic field \(H\) at low temperatures (2 K to 10 K) (insert in Figure 5) and is more informative. In each case \(M\) saturates at 2 K at values close to the expected saturation values for the respective number of Gd(III) sites but the increase of \(M\) vs. \(H\) is by far slower than one would expect for a Brillouin function calculated for \(S = 7/2\) para-magnetic centres. This again supports the evidence for weak antiferromagnetic interactions between the metal centres in all compounds.

**Monte Carlo simulations.** The size of the metal cages makes it impossible to model the magnetic behaviour using an exact quantum mechanical treatment based on a Heisenberg model approach since the Hilbert space dimension amounts to \((2S+1)^{N}\), where \(S\) is the spin quantum number for Gd and \(N\) is the number of Gd centres per cage. However, the cages are suitable for classical spin dynamics and Monte Carlo simulations based on a classical Heisenberg model where the Gd(III) centres are simulated by classical magnetic moments \(\vec{m}_{i}\); i.e. three dimensional vectors of length \(|\vec{m}_{i}| \propto \sqrt{S(S+1)}\).\(^{14}\) The Hamiltonian used for our simulations is given by
\[
H = -\frac{1}{2} \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \beta \sum_i \mu_i \mathbf{S}_i - \frac{\mu_0}{8\pi} \sum_i \mu_i (3(\mathbf{S}_i \cdot \mathbf{n})^2 - \mathbf{S}_i^2) \mathbf{n}_i
\]

Here, the first term contains the Heisenberg exchange interaction between two normalized magnetic moments \(\mathbf{S}_i\) and \(\mathbf{S}_j\). Therefore, the classical exchange constants \(J_{ij}\) have to be scaled with respect to the quantum values \(J_i\) by

\[
J_{ij} = J_i S(S + 1) = J_i \frac{63}{4}
\]

The second term is the Zeeman term which describes the interaction of each Gd centre with an external field (using the flux density \(B\)). The last term describes the classical dipole-dipole interaction which plays a significant role for very low temperatures in all Gd cages due to the large magnetic moment per ion. The determination of the classical exchange constants \(J_{ij}\) has been done by performing classical Monte Carlo simulations and fitting to the experimental \(\chi(T)\) data. In all cases, the contribution from the dipole-dipole interaction was found to be negligible for temperatures \(T > 2\) K. The obtained exchange-coupling constants were then used to calculate the \(M(B)\) curves and we find excellent agreement for all temperatures in the field range of \(0 < B < 4\) T. The exchange interactions found were: \(\text{Gd}_9\), \(-0.130\) K, \(\text{Gd}_{20}\), \(-0.030\) K; \(\text{Gd}_{15}\), \(-0.108\) K; \(\text{Gd}_{20}\), \(-0.127\) K; \(\text{Gd}_{60}\), \(J = -0.146\) K. For compound \(\text{Gd}_{15}\) four exchange interactions were needed to fit the data, i.e. \(J_1 = -0.165\) K, \(J_2 = -0.127\) K, \(J_3 = -0.063\) K, \(J_4 = -0.025\) K. Here, \(J_i\) describes the exchange interaction between nearest neighbours with the shortest distance. \(J_1, J_2,\) and \(J_4\) refer to exchange interactions between magnetic centers of larger distances.

The exchange coupling constant of \(\text{Gd}_{20}\) is significantly smaller when compared to the other systems, because the carbonate is a weak magnetic exchange bridge which was also observed previously in other systems. For higher fields there is a systematic deviation between experimental and theoretical results at lower temperatures, i.e. the theoretical curves lie above the experimental data. This is an artefact of the classical treatment, i.e. at saturation a classical spin of length \(\sqrt{S(S + 1)}\) can point completely in the field direction and is therefore larger than the corresponding quantum spin for which the maximum value is given by the quantum number \(m_s = S\). To the best of our knowledge, this is the first work where a classical Heisenberg model has been successfully used to model the magnetic properties of a rare earth magnetic molecule.

**Figure 5.** a-d) Plots of \(\chi T\) vs. \(T\) and isothermal magnetization curves (insets) and for \(\text{Gd}_9, \text{Gd}_{15}, \text{Gd}_{20}, \text{Gd}_{32}, \text{Gd}_{50}\) and \(\text{Gd}_{60}\), respectively. Dashed lines are the high-temperature limits for \(N\) non-interacting Gd(III) ions with \(g = 2.0\) in each compounds, respectively. The coloured lines display results from our classical Monte Carlo simulations (see text). The indicated black lines are calculated Brillouin functions for \(N\) magnetically isolated Gd(III) ions with \(S = 7/2, g = 2.0\) at \(T = 2\) K, respectively.

**Pulsed Magnetic Field Studies.** To further study the magnetic couplings obtained from Monte Carlo simulations we investigated the magnetization behaviors of these clusters using pulsed magnetic fields up to 10 T at very low temperatures. At 0.4 K and under adiabatic condition the magnetization takes a full-cycle sine wave shape for these complexes (Figure 6 and S8). In the down sweep from the highest field the magnetization gradually decreases for all of six complexes, but being higher than that in the first quarter up cycle due to the competition between the thermal relaxation and the fast change of the magnetic field. To further understand the magnetization behavior the differential magnetizations (dM/dB) are plotted against the pulsed field in Figure 6, which give clear magnetization steps (peaks in dM/dB vs B plots). For \(\text{Gd}_9\), these three peaks located at around 0, 0.9 T and 3.0 T, of which the
near-zero peak is much smaller compared to the others. For Gd$_{15}$, the two peaks are around 0 and 2.0 T. For Gd$_{20}$, one broad peak was observed at low field around zero, indicating the magnetic interactions are almost homogeneous in the system. For Gd$_{32}$, there are two peaks around 0 and 1.0 T. For Gd$_{50}$, there are two peaks located at around 0 and 1.9 T. For Gd$_{60}$, there are three distinct peaks around 0, 0.9 T and 2.5 T.

We reason that these peaks in the derivatives of magnetization indicate inequivalent magnetic superexchange-coupling interactions, for higher fields implying stronger magnetic interactions. Hence, we focus on the magnetic-structural correlation and try to elaborate the correlation between these peaks and structural geometries (see below). Magnetic exchange through carbonate and chloride are usually very weak,$^{15}$ and hence the peaks around the zero field in such as Gd$_{15}$, Gd$_{20}$, Gd$_{50}$ and Gd$_{60}$ are presumably caused by bridges of Cl$^{-}$ and CO$_{3}^{2-}$. The stronger exchange interactions seen are due to OH$^{-}$ or RO$^{-}$ bridges. To classify the Gd···Gd interactions through these groups, we made a survey in literature with reported magnetic exchange-coupling constants ($J$) of hydroxide-bridged Gd$^{III}$ clusters, many of which comprise similar building units such as triangles, squares, pyramid, octahedron and tetrahedron and show the Gd-O-Gd angles ($\phi$) are major structural factors that determine the magnetic interaction. The statistics of these angles and $J$ values are listed in Table S3, from which we can obtain an empirical relationship between them (Figure S9); a linear fitting provides the equation of $J = 0.0072\phi - 0.85245$ (cm$^{-1}$) ($80^\circ < \phi < 120^\circ$). Based on this expression, $\phi = 118.4^\circ$ is critical point that divides ferro or antiferro magnetic interactions.

![Figure 6](image_url)

Figure 6. The magnetic hysteresis plots at 0.4 K normalized by Gd(III) numbers, together with the field derivatives (dM/dB) vs B plots for Gd$^9$ (a), Gd$^{15}$ (b), Gd$^{20}$ (c), Gd$^{32}$ (d), Gd$^{50}$ (e) and Gd$^{60}$ (f).

For these series of Gd(III) complexes, the magnetic interactions are always antiferromagnetic as $\phi$ is usually smaller than 120$^\circ$ for OH$^{-}$ bridges. The correlation shows that the smaller the Gd-O-Gd angle the stronger the antiferromagnetic interactions. By analyzing the Gd-O-Gd angles and the peak positions in the dM/dB data we can attribute the following relationships: for $80^\circ$ – $96^\circ$, dM/dB peaks are around 2.5 – 3.0 T; for $96^\circ$ – $102^\circ$, peaks are around 2.0 – 2.5 T; for $102^\circ$ – $108^\circ$, peaks are around 1.0 – 2.0 T; for $108^\circ$ – $114^\circ$, peaks are around 0 – 1.0 T (for detail, see the grouped bond angles in different colors in “Summary of Gd-O-Gd angles and Gd···Gd separations of six Gd(III)-based cages” in Supporting Information). Interestingly, the four “absorption bands” in Gd$^{15}$ coincidently agree with the four magnetic superexchange-coupling constants suggested by the Monte Carlo simulations, though we are unable to correlate them one by one.

CONCLUSION

To summarize, a series of spherical Gd(III) cages and intermediate species with novel topologies were successfully isolated. Gd$_{20}$, Gd$_{50}$ and Gd$_{60}$ have approximate cubic or icosahedral symmetry while Gd$_{32}$ has exact $O_h$ symmetry. The geometry all six Gd(III) cages can be seen as combination of multiple polygons. The magnetism of these cages can be described by a simple classical Heisenberg model, providing the dominant antiferromagnetic interactions. Hence, many intriguing magnetic phenomena arising from geometrical spin-frustration may be expected in these systems.$^{17-24}$ This may pave a new way to obtain new molecular prototypes for the investigation of spin frustration, which will be a solid motivation for both synthetic chemists and theorists. Moreover, from the derivative of the magnetization analyses we can roughly correlate the peak bands and strengths of antiferromagnetic interactions. This may also be viewed as “fingerprints” of certain Gd cages, providing the opportunity to identify molecules under magnetic field.

EXPERIMENT SECTION
Synthesis. See supporting information.

Materials and Physical Measurements. All reagents are commercially available and were used as received without further purification. Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD area-detector diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. Absorption corrections were applied using multi-scan technique. Their structures were solved by direct method of SHELXTL and refined by full-matrix least-square techniques using the SHELXTL program. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Magnetic measurements (2-300 K) were carried out on powder samples by SQUID magnetometry (Quantum Design MPMS-XL). Diamagnetic corrections were calculated from Pascal constants. The measurements of the magnetization behaviors under the adiabatic condition at 0.4 K were done by using the pulsed magnetic field, which takes a full cycle.

ASSOCIATED CONTENT

Supporting Information.

Crystallographic information files (CIFs) and supporting tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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