Linked Supramolecular Building Blocks for Enhanced Cluster Formation

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 which naturally relies on targeted ligand composition. The serendipitous assembly through to rational design, the latter supported clusters, thereby demonstrating an enhanced and rational approach towards the targeted synthesis of complex and challenging structures.

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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] (H₈L₁) was synthesised according to literature procedure,[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 CH₂ bridges between phenyl rings impart flexibility that allows ring inversion to proceed in the solution phase with very low accompanying energy barriers.[14] Extension of this to H₈L₁ allows for the possibility that two sets of TBC[4] phenolic oxygen atoms may, upon rotation/inversion, orient such that they are directed towards 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 H₈L₁ would allow us to controllably introduce multiple metal centres of predetermined oxidation states (e.g., two [MnIII-TBC[4]] moieties) in order to enhance the formation of new polynuclear metal clusters.

Results and Discussion

Reaction of H₈L₁ with manganese(II) chloride hydrate in a DMF/MeOH mixture and in the presence of base afforded single crystals of [MnIII₄MnII₄(L₁)₂(NO₃)₂(NO₃)(Cl) (H₂O)(MeOH)(dmf)]·2H₂O·12MeCN (1), following slow diffusion with acetonitrile (Figure 2).[15] The isolated complex contains a mixed valence MnIII₄MnII₄ cluster that is strikingly similar to the archetypal MnIII₂MnII₂ butterfly motif isolated with TBC[4].[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 MnIII ions into a cluster. Furthermore, additional binding sites between the TBC[4] fragments in each L₁ are occupied by MnII ions. The structure of 1 is best described as two L₁-supported distorted MnIII₂MnII₂ butterflies, or alternatively as two MnIII₄-TBC[4] metalloligands encapsulating two “naked” MnII ions. The metal ions are linked together by bridging phenolates, hydroxide and chloride (or formate[15] generated by in situ hydrolysis of dmf). The metal core and coordination environment relating to each “Mn₄” (Mn₁–Mn₄ cf. Mn₅–Mn₈) is essentially the same, and so only one half of the metal cluster will be described in detail. Mn₁ is centrally bound to four fully deprotonated phenolic oxygen atoms O₁–O₄ (Mn–O range 1.865(3)–1.956(3) Å) of one TBC[4] moiety. As

![Figure 1. Selected polymeric TBC[4]-supported clusters and the related bridge-linked bis-TBC[4]. A) Clusters supported by two TBC[4]s with tailored metal composition (MnIII₄MnII₄LnIII₆).[4, 5, 9, 12] B) Square within square MnIII₄LnMIII₄ clusters supported by four TBC[4]s.[6, 7] C) Tricapped trigonal prismatic Cu₉ cluster motif with anions and ligated solvent omitted for clarity.[10] D) Metallic skeletons of clusters shown in A–C with capping TBC[4]:TM/LnM moieties drawn as large spheres. E) Two views of bis-TBC[4] showing the antiparallel arrangement and hydrogen-bonding interactions at the TBC[4] lower-rims. Colour code: Mn, purple; Ln, green; Cu, pale blue; N, royal blue; C, grey; O, red; S, yellow; H atoms are omitted for clarity.](image-url)
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-O17 2.104(4) Å) and two 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 each have quarter occupancy (Mn3-O24 2.196(5) Å). 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 “Mn8 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 Mn8 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 H1,L1 with manganese(II) chloride and gadolinium(III) chloride in a DMF/MeOH mixture in the presence of base afforded single crystals of formula [Mn16,Gd4,Cl4,16L1-8H]2(Cl)2[(μ3-OH)4(MeOH)2(dmf)8](Et2O)5(dmf)2 upon slow diffusion with diethyl ether (Figure 3). Structural analysis reveals, as predicted, that each TBC[4] fragment contains an Mn8 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 Mn11 for one Gd11 in the binding site located between the two TBC[4] cavities of each L1. The central core is best described as a central Mn8,Gd4 butterfly motif that is edge fused (sharing one Mn11 ion and one Gd11 ion) to two symmetry equivalent (s.e.) peripheral Mn11,Gd11 butterflies; Mn11,TBC[4] moieties are again found to encapsulate “naked” Mn8 and Gd4 ions. The central butterfly contains two s.e. distorted octahedral Mn11 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 μ-hydroxide (Mn3-O9 2.162(4) Å). The O(dmf)-Mn3-Ο-Mn11 ) vector defines the Jahn–Teller axes with significant deviation from linearity (164.7(2)°). The central Gd11 ions (Gd1 and s.e.) are located in the binding sites situated between the two TBC[4] cavities. B) Polymetallic core of 1 showing the two butterfly units linked through phenolate, chloride and hydroxide bridging. C) Detailed view of one butterfly within 1. D) Metallic skeleton of 1 showing the two butterfly units linked through phenolate, chloride and hydroxide bridging. C) Detailed view of one butterfly within 1.

![Figure 2. Views of the single-crystal X-ray structure of 1 showing the polymetallic Mn8,Mn8 core. A) Cluster in 1 showing acetonitrile molecules in space-filling representation occupying the bis-TBC[4] cavities. B) Polymetallic core of 1 showing the two butterfly units linked through phenolate, chloride and hydroxide bridging. C) Detailed view of one butterfly within 1. D) Metallic skeleton of 1 showing the two butterfly units linked through phenolate, chloride and hydroxide bridging. C) Detailed view of one butterfly within 1.](image-url)
and Gd1–O9' 2.362(4) Å, respectively), and to a second μ-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 μ-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 μ-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 [CuII(OH)(MeCN)14(dmf)7]·(OH)(MeCN)4 (3) following diffusion of acetonitrile (Figure 4). Structure analysis reveals a CuII cluster supported by two inverted L1 ligands. The TBC[4] pockets and additional binding sites are all occupied by CuII ions (Figure 4 A). The two CuII-L1 moieties are connected by four additional CuII ions (Figure 4 B), giving a polynuclear core that conforms to a tetracapped diamond (or tetracapped square prism). Each face is thus capped by a TBC[4]-CuII moiety, with the overall framework bearing obvious similarity to the tricapped trigonal prismatic CuII clusters isolated from analogous reactions with TBC[4] (Figure 1 C). That is, the latter describes three CuII-TBC[4] metalloligands encapsulating a trigonal prism, and the former describes four CuII-TBC[4] metalloligands encapsulating a square prism. The remaining CuII ion in 3 resides in the centre of the prism and is disordered over several positions. The four capping CuII 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)–1.976(5) Å). Four distorted square planar CuII 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 CuII 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 CuII 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 CuII ion. These five CuII ions are interconnected by a combination of five μ-OH ligands giving a cationic cluster.

The TBC[4],CuII 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 CuII2 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 Cu13 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$^3$mol$^{-1}$K for 1 is lower than the value of 29.5 cm$^3$mol$^{-1}$K, expected for spin-only contributions to the magnetism, assuming $g = 2.0$ for both Mn$^{II}$ and Mn$^{III}$, $g$ 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$^3$mol$^{-1}$K at 5 K. The spin-Hamiltonian matrix of 1 is a square matrix of dimension 810,000 and cannot be diagonalised by standard
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\(^{[19]}\) 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:

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

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, $\mathbf{S}_i$ is a single-ion spin operator, and $J$ is the isotropic exchange parameter between a pair of metal centres. To avoid over-parameterisation we have assumed that all Mn$^{\text{II}}$–Mn$^{\text{II}}$, all Mn$^{\text{II}}$–Mn$^{\text{III}}$ and Mn$^{\text{III}}$–Mn$^{\text{III}}$ isotropic exchange parameters are the same. This results in three independent fit parameters to account for the pairwise isotropic exchange interaction terms: $J_{1-2, 2-3, 3-4, 4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12, 12-13}$ between Mn$^{\text{II}}$ and Mn$^{\text{III}}$ centres (hereafter referred to as $J_{\text{Mn}^{\text{II}}, \text{Mn}^{\text{III}}}$); $J_{1-2, 2-3, 3-4, 4-5}$ between Mn$^{\text{II}}$ centres ($J_{\text{Mn}^{\text{II}}, \text{Mn}^{\text{II}}}$); and $J_{4-5}$ between Mn$^{\text{III}}$ centres ($J_{\text{Mn}^{\text{III}}, \text{Mn}^{\text{III}}}$). These pairwise isotropic exchange parameters are schematically represented in the insets of Figure 5. Under these conditions, the best-fit parameters for $2$ are: $J_{\text{Mn}^{\text{II}}, \text{Mn}^{\text{III}}} = +0.92 \text{ cm}^{-1}$, $J_{\text{Mn}^{\text{II}}, \text{Mn}^{\text{II}}} = -4.48 \text{ cm}^{-1}$ and $J_{\text{Mn}^{\text{III}}, \text{Mn}^{\text{III}}} = -1.52 \text{ cm}^{-1}$. The best-fit curve is shown in Figure 5. These values are in good agreement with the parameters previously determined for molecules containing the same inverted butterfly topology of Mn$^{\text{II}}$ and Mn$^{\text{III}}$ centres.\(^{[4,5,21]}\) With these parameters, the ground spin-state of $1$ is a singlet ($S = 0$), with numerous excited spin-states lying in very close proximity (Figure S11 in the Supporting Information).

At 300 K, the $\chi_{MT}$ value of 38.0 cm$^3$ mol$^{-1}$ K for $2$ is slightly higher than the value of 36.5 cm$^3$ mol$^{-1}$ K, expected for spin-only contributions to the magnetism of $2$, assuming $g = 2.0$ for Mn$^{\text{II}}$, Mn$^{\text{III}}$ and Gd$^{\text{III}}$. On lowering the temperature, the $\chi_{MT}$ product of $2$ remains constant down to $T = 150$ K wherefrom it begins to increase, reaching a maximum value of 53.2 cm$^3$ mol$^{-1}$ K at 7 K. The spin-Hamiltonian matrix of $3$ is a square matrix of dimension 8,192 and is much easier to handle than the spin-Hamiltonian matrices of $1$ and $2$. Thus, we measured variable-field and variable-temperature (VTVB) magnetisation data in the temperature range 2 to 7 K and in the magnetic field range 0.5 to 5 T. The variation of the $\chi_{MT}$ product and the VTVB data were simultaneously fitted to isotropic spin-Hamiltonian \(^{[11]}\), which remains an appropriate model for the magnetic properties of $3$, since single-ion anisotropy terms here are zero ($\text{Cu}^{\text{II}} = S = 1/2$). We chose to neglect antisymmetric interaction terms, often used for the interpretation of the magnetic properties of Cu$^{\text{II}}$-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 \(^{[11]}\) (Equation (1)) (Figure 5): $J_{1-2, 2-3, 3-4, 4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12, 12-13}$ are used to take into account the exchange between Cu$^{\text{II}}$ centres bridged by hydroxides ($J_1$; the vertices of the square prism); $J_{1-2, 2-3, 3-4, 4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12, 12-13}$ are used to take into account the exchange between the Cu$^{\text{II}}$ ions around the peripheral Cu$^{\text{II}}$ “wheel” ($J_2$) and finally $J_{1-2, 2-3, 3-4, 4-5, 5-6, 6-7, 7-8, 8-9, 9-10, 10-11, 11-12, 12-13}$ are used to take into account the exchange between the central Cu$^{\text{II}}$ 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.\(^{[23,24]}\)

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$\text{[4]}$, which itself can be regarded as a versatile ligand for polymeric cluster construction (Figure 1). The appropriate combination of two (or more) conjoined ligands is an important step towards
enhanced control over topology, nuclearity and properties of polymeric clusters with these building blocks. Indeed the magnetic exchange between the constituent metal ions in complexes 1–3 is very much akin to that observed in molecules built form TBC[4]. Given the large library of TBC[4] clusters known, the correlation between structure and magnetism in novel bis-TBC[4] cages can become more targeted. Work continues in the controlled construction of polymeric clusters with bis-TBC[4], the results of which will be reported in due course.

Experimental Section

Bis-TBC[4] (H2L1) was synthesised according to literature procedure.13 Crystal data for bisTBC[4]·(CHCl3)4: C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14. Yield (108 mg, 27%); elemental analysis (%) calcd for C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14: C 25.60, H 3.41, N 5.75; found: C 25.58, H 3.39, N 5.72.

Synthesis of [MnIII4MnII4(L1)2(μ3-OH)2(μ-Cl)(H2O)6(MeOH)3]·(DMF)4 (1)

H2L1 (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 acetone, the resulting crystals were filtered and dried.

Crystal data for 1: C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14: M = 4451.01, dark green block, 0.32 × 0.30 × 0.23 mm3, monoclinic, space group P21/c (No. 14), α = 16.73(1), b = 30.60(6), c = 21.743(4) Å, β = 101.89(3)°, V = 10890(4) Å3, Z = 2. Neutron diffraction studies were performed using single-crystal X-ray diffraction studies were grown by vapour diffusion of the mother liquor with acetonitrile. Yield (81 mg, 21%); elemental analysis (%) calcd for C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14: C 25.60, H 3.41, N 5.75; found: C 25.58, H 3.39, N 5.72.

Synthesis of [MnIII4MnII4·(L1–BH)2(μ3-OH)2(μ-Cl)(MeOH)2](dmf)2·(Et2O)(dmf) (2)

H2L1 (200 mg, 0.172 mmol), MnCl2·4H2O (68 mg, 0.344 mmol) and GdCl3·6H2O (64 mg, 0.172 mmol) were stirred in a solution mixture of DMF/MeOH (12 mL:12 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: C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14: M = 4451.01, dark green block, 0.32 × 0.30 × 0.23 mm3, monoclinic, space group P21/c (No. 14), a = 16.73(1), b = 30.60(6), c = 21.743(4) Å, β = 101.89(3)°, V = 10890(4) Å3, Z = 2. Neutron diffraction studies were performed using single-crystal 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: C26H32Cl2Gd2Mn6N16O36·(H2O)2·(MeCN)14: C 25.60, H 3.41, N 5.75; found: C 25.58, H 3.39, N 5.72.
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