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ARTICLE TYPE

A pseudo-icosahedral cage {Gd$_{12}$} based on aminomethylphosphonate

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Reaction of (aminomethyl)phosphonic acid (ampH$_2$) with a mixture of gadolinium and cobalt pivalates under solvothermal conditions, led to a pseudo-icosahedral cage {Gd$_{12}$}, which shows a large magnetocaloric effect (MCE).

10 Metal phosphonate clusters have been extensively studied for their fascinating structures and interesting magnetic properties.[1] 3d–4f heterometallic cages[2] and more recently lanthanide (4f) homometallic[3] phosphonate clusters have been studied because of the range of magnetic anisotropies of the lanthanide ions and the 15 weak coupling between the metal sites can produce unusual and potentially useful physics.[4] Some cages such as {Dy$_2$},[3b] {Dy$_4$}[3d] and {Cu$_{24}$Dy$_8$},[2a] are single molecule magnets (SMM) because of the very anisotropic Dy^{III} ions.[5] When the isotropic Gd^{III} ion is present, phosphonate clusters[2c-h] display impressive 20 magnetocaloric effects (MCE), which have been proposed for application in magnetic refrigeration.[6] For example, the observed magnetic entropy changes of a series of Co–Ln phosphonate grids and cages[3d] range from 20.0 to 28.6 J kg^{-1} K^{-1} for a magnetic field change ΔH = 70 kG and 3 K, while the highest magnetic entropy 25 change is 33.7 J kg^{-1} K^{-1} found for {Mn$^{II}_4$Gd$^{III}_6$}[3e] for ΔH = 70 kG and 3 K.

Previous studies have shown that the phosphonate moiety is an efficient functional group for the construction of molecular cages.[7] Another frequently used ligand to prepare the polynuclear 30 3d–4f and 4f clusters is α-amino acids.[8] Given this extensive body of previous work we thought that (aminomethyl)phosphonic acid (ampH$_2$, Scheme 1), which is the smallest α-amino phosphonic acid, should be a useful ligand to synthesize 3d–4f and 4f cages.

35 Here we report our first explorations using ampH$_2$ which have resulted in a dodecanuclear pseudo-icosahedral gadolinium cage. Firstly, ampH$_2$ was dissolved in mixed solvent of MeOH/H$_2$O and deprotonated by NEt$_3$ to give a clear solution. Then [Gd$^{III}_2$(O$_2$C^{t}Bu)$_6$(HO$_2$C^{t}Bu)$_6$] and [Co$^{II}_2$(μ- 40 OH$_2$)(O$_2$C^{t}Bu)$_4$]·(HO$_2$C^{t}Bu)$_4$ were mixed and stirred in MeCN to generate a suspension. Reaction of the resulting solution and suspension under solvothermal conditions, followed by cooling to room temperature, gave light pink crystals of (HNEt$_3$)$_4$[Co^{II}(H$_2$O)$_6$(H$_3$NCH$_2$PO$_3$)$_{12}$Gd$^{III}_{12}$(O$_2$C^{t}Bu)$_{24}$(OH)$_6$] 45 ·8MeCN·18H$_2$O (**1**·8MeCN·18H$_2$O).
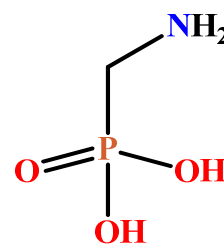
Scheme 1 the structure of ampH$_2$ ligands.

The X-ray crystal structure analysis shows that compound **1** crystallizes in the tetragonal space group $P4_2/mmc$ and the 50 molecular skeleton takes a shape of a pseudo-icosahedral cage, with a Co^{II} hexahydrate cation trapped in the center of the molecule (Fig. 1). The molecule has 222 crystallographic symmetry with three twofold axes intersecting at the center of the molecule at the Co^{II} ion site. As a result, only three of the Gd^{III} 55 ions and three of the ampH$^-$ ligands are crystallographically independent. The molecule also exhibits non-crystallographic triangular and pentagonal symmetry (Fig. S1). Each of ten threefold pseudo-axes traverses the center of two {Gd$_3$} triangles while the six fivefold pseudo-axes pass through Gd, Co and Gd' 60 sites. A previously reported cluster [Cp$_{12}$Sm$_{12}$(μ$_3$-Cl)$_{24}$] (Cp = η^5-C$_5$H$_5$) possesses similar symmetrical features.[9] Due to the regularlity of the structure the phosphorus atoms are also arranged in an icosahedron (Fig. S2).

The ampH$^-$ ligand links three Gd^{III} ions using the 3.111 65 binding mode (Fig. 2), with the nitrogen atom uncoordinated. Six μ-OH groups bridge six pairs of Gd^{III} ions, respectively. Two ^{t}BuCOO$^-$ ligands chelate to each Gd^{III} ion. Therefore, all of the Gd^{III} ions are eight-coordinate with distorted triangular dodecahedral geometries, formed by four oxygens of two 70 ^{t}BuCOO$^-$ ligands, three oxygens of three ampH$^-$ ligands, and one oxygen of an OH group. The Gd−O bond lengths are in the range of 2.258−2.565 Å, comparable to the values found for previous gadolinium-containing phosphonate clusters.[2] The shortest Gd···Gd contacts are 4.553−4.625 Å and are those bridged by μ-75 OH groups with Gd−O−Gd' angle of 128.75−132.61° (Fig. 2). These separations are longer than those found for similar μ-OH-bridged Gd^{III} clusters *ca*. 3.8 Å,[10] which may result in weaker magnetic interaction between Gd^{III} ions. The longer Gd···Gd separations are bridged by ampH$^-$ ligands (e.g. Gd1···Gd3 in Fig. 80 2) and are in the range of 6.874−6.898 Å. The Co^{II} ion is coordinated by six water molecules which are disordered over

eight positions, with Co−O bond lengths of 2.083 Å. The Co···Gd distances are *ca.* 6.0 Å. The isolated Co^{II} hexahydrate cation filling the cavity in the cage is crucial to stabilize the whole molecule, as water molecules are interacting with the cage by hydrogen bonding. No identifiable products or crystals are obtained if the reaction is carried out in the absence of the cobalt pivalate complex.
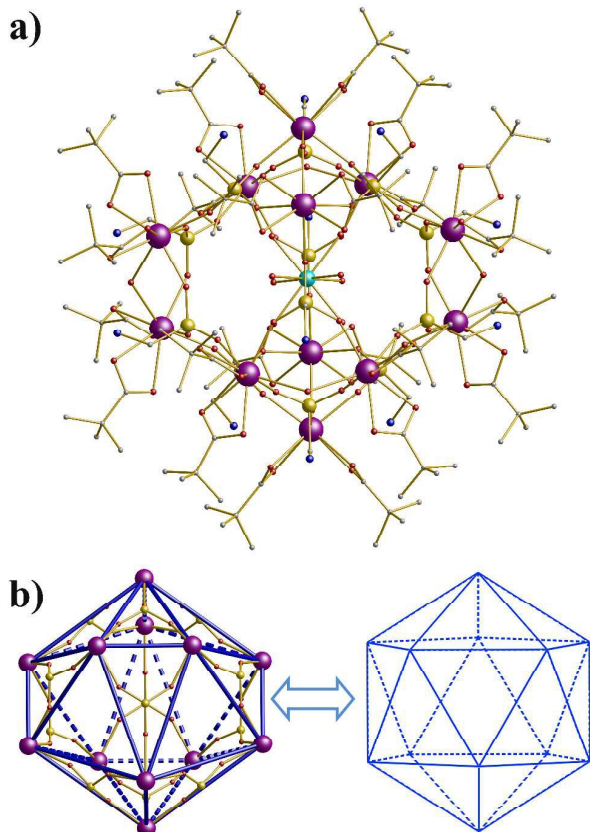
a)

b)

Fig. 1 (a) Ball and stick plot of compound **1**, excluding hydrogen atoms. Colour code: Gd: violet, Co: turquoise, P: gold, O: red, N: blue and C: grey. (b) Structure of the {Gd$_{12}$(PO$_3$)$_{12}$} skeleton of **1** (left) compared to a regular icosahedron (right). Sticks linking Gd atoms are only guides to the eye.
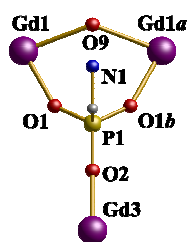

Fig. 2 Coordination modes of the ampH$^−$ ligands and the OH$^−$ ligands in **1**, excluding hydrogen atoms.

The closest Gd···Gd separation between neighbouring molecules is *ca.* 10.6 Å, which preclude any significant intermolecular interactions. Space-filling representations demonstrate that the overall molecule of compound **1** is in a spherical shape with a approximate diameter of 2.0 nm (Fig. S3). The packing of molecules generates two types of one-dimensional square channels in the *c* axis direction with diagonal separations of 1.3 and 1.1 nm (Fig. S4), respectively.

Variable-temperature (2−300 K) magnetic susceptibility data were collected for polycrystalline samples of compound **1** in an applied direct-current (dc) magnetic field of 5 kG (Fig. 3). The room-temperature $\chi_M T$ value for **1** is 94.0 cm^3 K mol^{-1}, which is in agreement with the theoretically expected value of 96.4 cm^3 K mol^{-1} for spin-only twelve Gd^{III} ($S = 7/2$, $g = 2$) and one Co^{II} ($S = 3/2$, $g = 2$).[4a] Upon lowering the temperature, $\chi_M T$ values decrease gradually to 90.4 cm^3 K mol^{-1} at 10 K and then fall abruptly to a minimum of 78.7 cm^3 K mol^{-1} at 2 K. The overall magnetic behaviour is due in the main to the cobalt(II) ion, where the orbitally degenerate ground state will show signnificant temperature dependent behaviour. There may be antiferromagnetic interactions between the Gd···Gd ions bridged by hydroxides, but this cannot be modelled sensibly due to the presence of the six-coordinate Co^{II} ion.
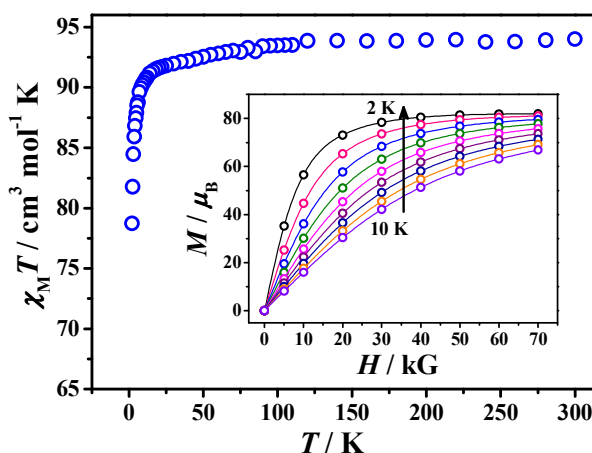

Fig. 3 Plot of temperature dependence of $\chi_M T$ for **1** in a 5 kG dc field at the range of 2−300 K. Inset: field dependence of the magnetization at indicated temperatures (2−10 K) for **1**. Lines are visual guides only.

Magnetization measurements on compound **1** were performed at the 2−10 K temperature range under 0−70 kG field (Fig. 3 inset). The *M vs*. *H* data display a steady increase in magnetization to reach 81.9 μ_B at 70 kG at 2 K without achieving saturation. This value is a little lower than the value that would be expected for twelve isolated Gd^{III} ions (*ca.* 83.6 μ_B), which suggests some weak anti-ferromagnetic exchange are present. Given the large magnetization values, we investigated the magnetocaloric properties for compound **1**. The magnetic entropy change can be estimated from the magnetization change as a function of applied field and temperature (Fig. 4) by using the Maxwell equation $\Delta S_m(T) = \int[\partial M(T,H)/\partial T]dH$. The resulting maximum magnetic entropy change is 26.7 J kg^{-1} K^{-1} for $\Delta H = 70$ kG at 2 K. This value is comparable to reported 3d–4f phosphonate clusters.[6]
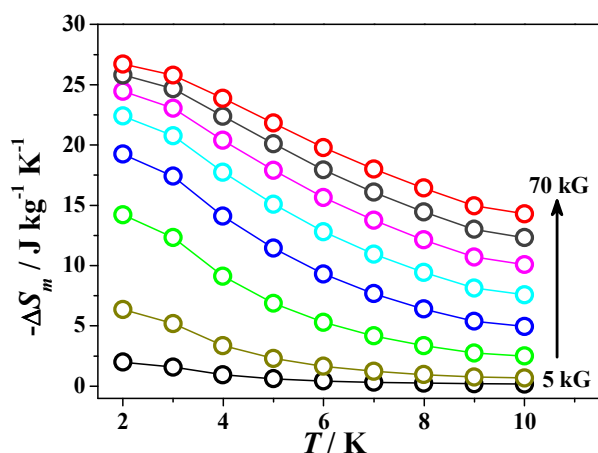
Fig. 4 $-\Delta S_{m}(T)$ calculated from magnetization data of **1** at various fields (5−70 kG) and temperature (2−10 K).

In summary, we have shown that (aminomethyl)phosphonic acid reacts with gadolinium and cobalt pivalates to give a pseudo-icosahedral cage {Gd$_{12}$}. The molecular skeleton, including twelve Gd ions and twelve P atoms, possesses a fascinating icosahedron-in-icosahedron topology. Magnetic studies revealed that the compound exhibits a large MCE at the ultralow temperature. The present work suggests that ampH$_2$ is an efficient ligand to construct 4f cages. Further studies on 4f and 3d–4f phosphonate cages using ampH$_2$ are in progress.

The icosahedron is Platonic solid, and the presence of five-membered metal rings should lead to significant frustration effects.[11] Unfortunately, the presence of the divalent Co site prevents informative magnetic studies of this polyhedron in this case. This is particularly unfortunate as there have been very interesting recent reports of spin frustration effects in gadolinium cage complexes.[12] We are attempting to synthesise the analogue of compound **1** with a diamagnetic divalent ion at the centre.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, X-ray crystallography and structural figures. CCDC 1450005. For ESI and crystallographic data in CIF format see DOI: 10.1039/c0xx00000x.

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