Supporting Information

A pseudo-icosahedral cage $\{Gd_{12}\}$ based on aminomethylphosphonate

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Experimental details

General Remarks: Commercially available chemicals were used as received without further purification. Crystallographic measurements for **1** were carried out with the Agilent SUPERNOVA diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. The structure was solved by direct methods using ShelXS and were refined by full-matrix least-squares methods using ShelXL and Olex2. Magnetic data were measured with a Quantum Design MPMS-XL7 SQUID magnetometer. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

Synthesis of precursors: $[Gd^{III}_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ and $[Co^{II}_2(\mu\text{-}OH_2)(O_2C^tBu)_4]\cdot(HO_2C^tBu)_4$ were synthesized according to the reported methods.[1,2]

Synthesis of 1: $[Co^{II}_2(\mu\text{-}OH_2)(O_2C^tBu)_4(HO_2C^tBu)_4]$ (0.048 g, 0.05 mmol), $[Gd^{III}_2(O_2C^tBu)_6(HO_2C^tBu)_6]$ (0.154 g, 0.1 mmol) and MeCN (8 mL) were mixed and stirred for ten minutes at room temperature. $NH_2CH_2PO_3H_2$ (0.011 g, 0.1 mmol) was dissolved in mixed solvent of MeOH/H_2O (0.1/0.1 mL) with Et_3N (0.1 mL, 1.0 mmol) as base. The resulting mixtures were transferred into a 10 mL Teflon-lined autoclave and then heated at 150^{o}C for 12 hours and afterwards cooled to room temperature at a rate of 0.05^{o}C min^{-1}. Light pink prism-shape crystals were collected (yield 22 % based on P), then washed with MeCN and dried in air. IR: 2959 (br), 2868 (br), 1525 (s), 1483 (s), 1424 (s), 1360 (s), 1225 (m), 1116 (vs), 1018 (s), 937 (w), 896 (m), 807 (w), 795 (w), 739 (w), 672 (w), 605 (m). Elemental analyses $C_{172}H_{418}CoGd_{12}N_{24}O_{114}P_{12}$ found (calcd) % : C 29.98 (29.66), H 5.91 (6.05), N 4.90 (4.83), P 5.24 (5.33), Co 0.97 (0.85), Gd 26.99 (27.09).

Crystallographic details: $C_{172}H_{418}CoGd_{12}N_{24}O_{114}P_{12}$, M = 6964.8, Tetragonal, space group $P4_2/mmc$, $a = b$ = 28.0168(10) Å, c = 21.7936(7) Å, $\alpha = \beta = \gamma$ = 90°, V = 17106.7(13) Å^3, T = 100(2) K, Z = 2, 35717 reflections collected, 8391 reflections used (R_{int} = 0.0520), R_1 = 0.0803 ($I > 2\sigma(I)$), wR_2 = 0.2654 (all data), GoF = 1.008. CCDC 1450005. $[HNEt_3]^+$ cations are assumed based on the charge balance, but not revealed crystallographically. Some severely disordered guest molecules have been removed by the SQUEEZE program in course of structural refinement. The hydrogens of ligands $NH_3CH_2PO_3$ are absent due to threefold disordered of aminium.

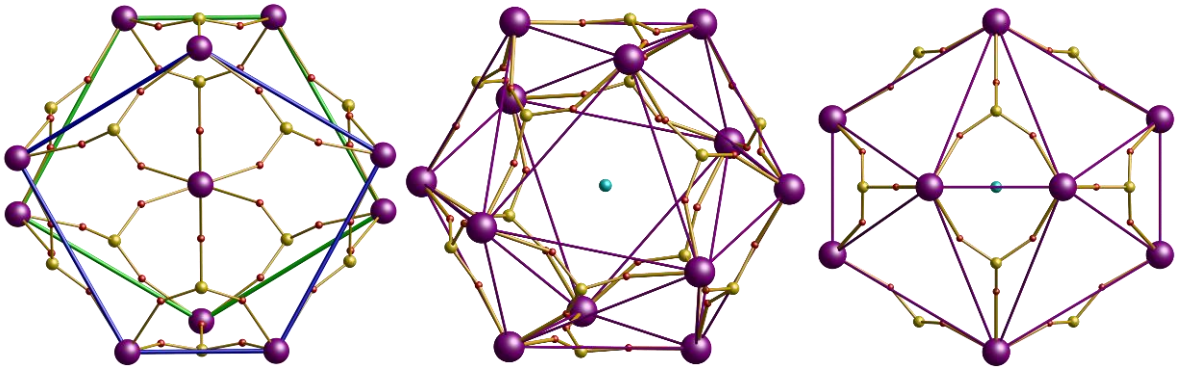

Fig. S1 Structures of the $\{Gd_{12}(PO_3)_{12}\}$ skeleton of **1** viewed along the fivefold pseudo-axes (left), the threefold pseudo-axes (middle) and the twofold axes (right). Sticks linking Gd atoms are only guides to the eye.

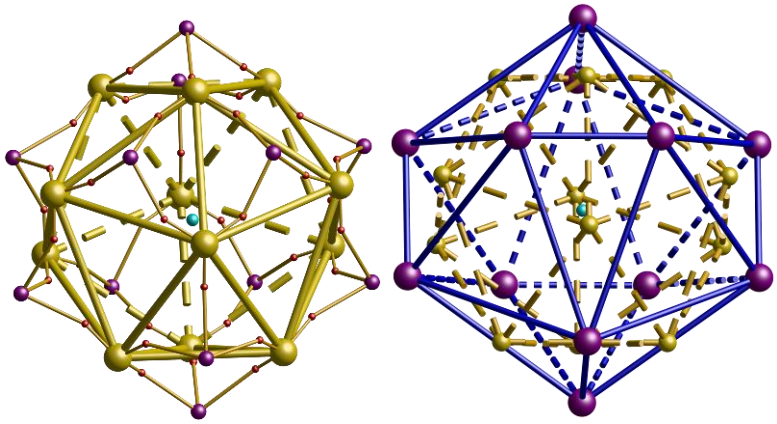

Fig. S2 Structures of the $\{Gd_{12}(PO_3)_{12}\}$ skeleton of **1** shows the icosahedral arrangement of P atoms (left) and the icosahedron-in-icosahedron topology(right). Sticks linking P and Gd atoms are only guides to the eye.

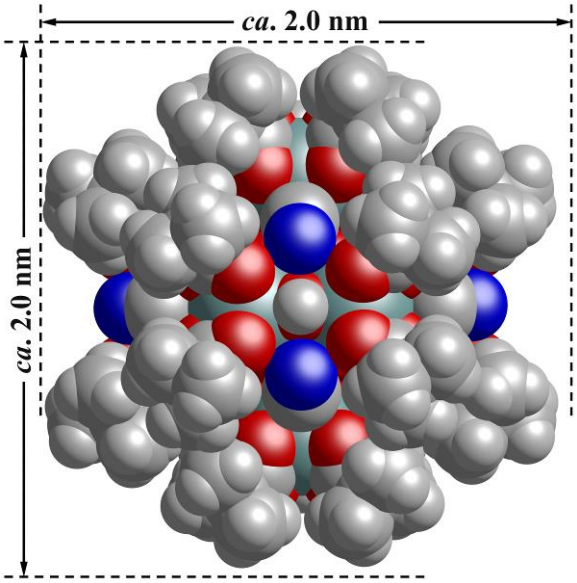

Fig. S3 Space-filling representation (including hydrogen atoms) viewed along the *c* axis for compound **1**, showing the diameter of the spherical molecular cage.

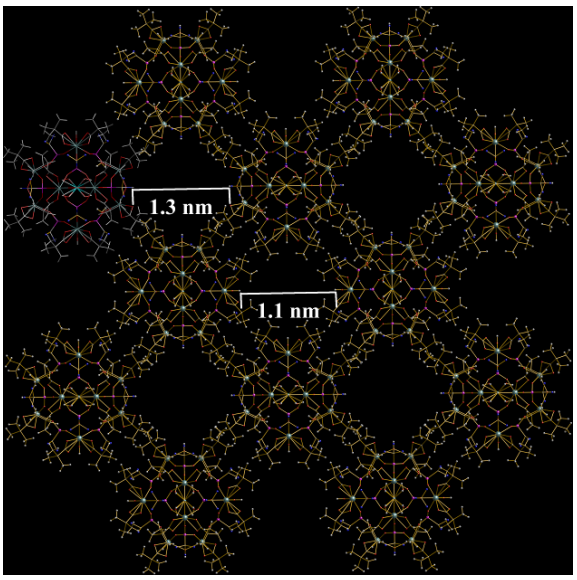

Fig. S4 Ball and stick plots of compound **1** (including hydrogen atoms) viewed along the *c* axis, showing the sizes of two types of one-dimensional square channels.

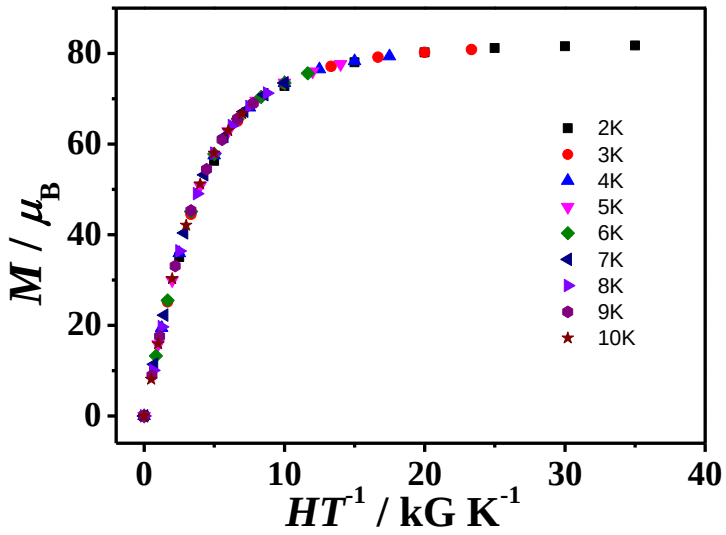

Fig. S5 Plot of *M* vs. HT^{-1} at indicated temperatures (2−10 K) for **1**.

Reference:

1 (*a*) I. G. Fomina, M. A. Kiskin, A. G. Martynov, G. G. Aleksandrov, Z. V. Dobrokhotova, Y. G. Gorbunova, Y. G. Shvedenkov, A. Y. Tsivadze, V. M. Novotortsev and I. L. Eremenko, *Zh. Neorg. Khim.*, 2004, **49**, 1463; (*b*) T. A. Zoan, N. P. Kuzmina, S. N. Frolovskaya, A. N. Rykov, N. D. Mitrofanova, S. I. Troyanov, A. P. Pisarevsky, L. I. Martynenko and Y. M. Korenev, *J. Alloys Compd.*, 1995, **225**, 396.

2 (*a*) D G. Aromi, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Chem. Eur. J.*, 2003, **9**, 5142; (*b*) G. Chaboussant, R. Basler, H.-U. Gudel, S. T. Ochsenbein, A. Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco and R. E. P. Winpenny, Dalton Trans., 2004, 2758