

Electronic Supplementary Information

A Nanosized Gd₆Ni₃ Cluster-Based Heterometallic Coordination

Polymer

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Materials and methods. All reagents were of commercial origin and were used as received. Aqueous solution of gadolinium perchlorate was prepared by digesting gadolinium oxide in concentrated perchloric acid. A suitable concentration was achieved by dilution of the concentrated solution with deionized water. The hydrothermal synthesis was carried out in polytetrafluoroethylene lined stainless steel containers under autogenous pressure. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectrum was recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curve was prepared on a SDT Q600 Thermal Analyzer. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). AC impedance measure was performed by use of 2-wire mode on the WAYNE KERR 6500 High Frequency LCR Meter. The frequency range of AC source is from 50 Hz to 50 MHz. The amplitude of AC source is 1V. The powdered sample was compressed to pellet with the size of $0.90\text{ mm}^2 \times 0.35\text{ mm}$. Two test lines were fixed on the tableting via electric glue and connected with the apparatus. The temperature-controlled apparatus is Sigma/Delta instrument. The X-ray powder diffractometry (PXRD) was performed with a Panalytical X-Pert PRO diffractometer with Cu-K α radiation ($\lambda = 0.15418\text{ nm}$, 40.0 kV, 30.0 mA).

Six types of coordination modes of Gd³⁺ ions in complex 1. Gd1 within cluster of Gd₆Ni₃ is connected by nine oxygen atoms from three phosphate groups in unidentate fashion and three phosphate groups in bidentate chelating fashion, displaying tricapped trigonal prism coordination geometry. Gd2, bridged with the adjacent Gd₆Ni₃ clusters, features heptacoordinated capped trigonal prism coordination geometry, which contribution of two phosphate oxygen atoms from two [PMIDA]⁴⁻ ligands, two carboxylate atoms from other two [PMIDA]⁴⁻ ligands and three aqua ligands. Nonacoordinated Gd3 is chelated by two [PMIDA]⁴⁻ ligands in tetradentate fashion, and the rest coordination sphere is fulfilled another phosphate oxygen atoms. Gd4 locates in the center of capped square antiprism geometry and is chelated by one [PMIDA]⁴⁻ ligand in tetradentate fashion, one phosphate oxygen, one carboxylate atom and three aqua ligands. Gd5 adopts a capped square antiprism geometry and is coordinated by two carboxylate atoms from one carboxylate group in chelating mode, one phosphate oxygen atom and six aqua ligands. Gd6 is octacoordinated, with contribution of two phosphate oxygen atoms, one carboxylate atoms and five aqua ligands.

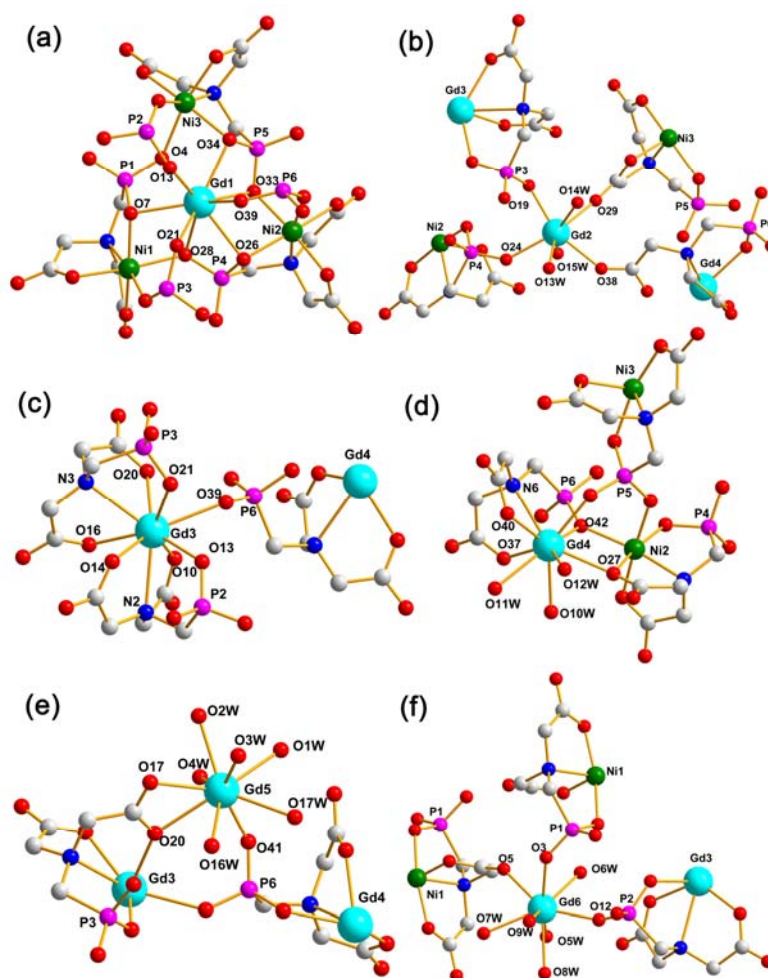


Fig. S1 The coordination modes of Gd1, Gd2, Gd3, Gd4, Gd5 and Gd6.

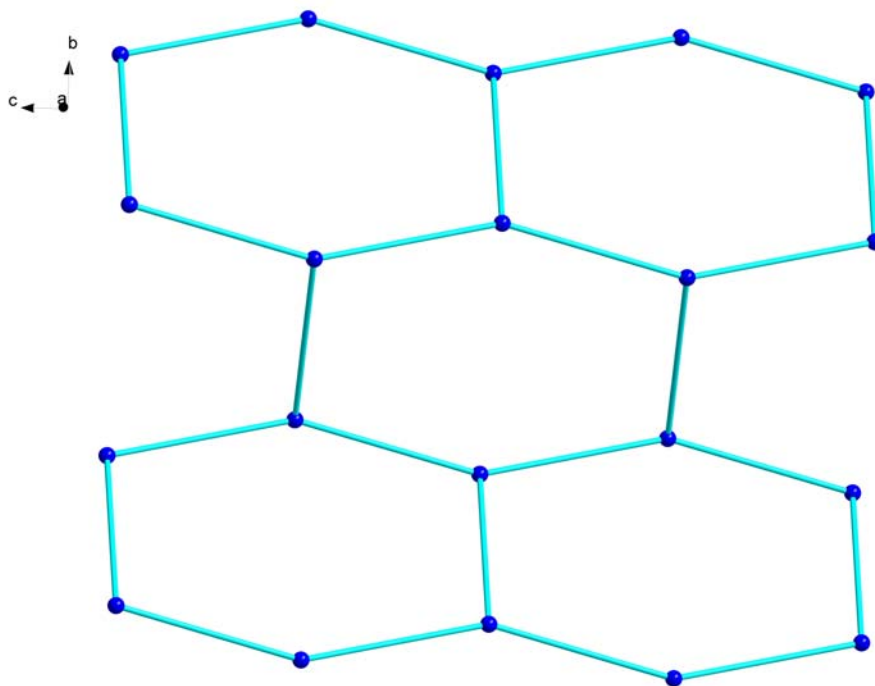


Fig. S2 The 2D 6³-network of **1** based on the Gd₆Ni₃ clusters as node.

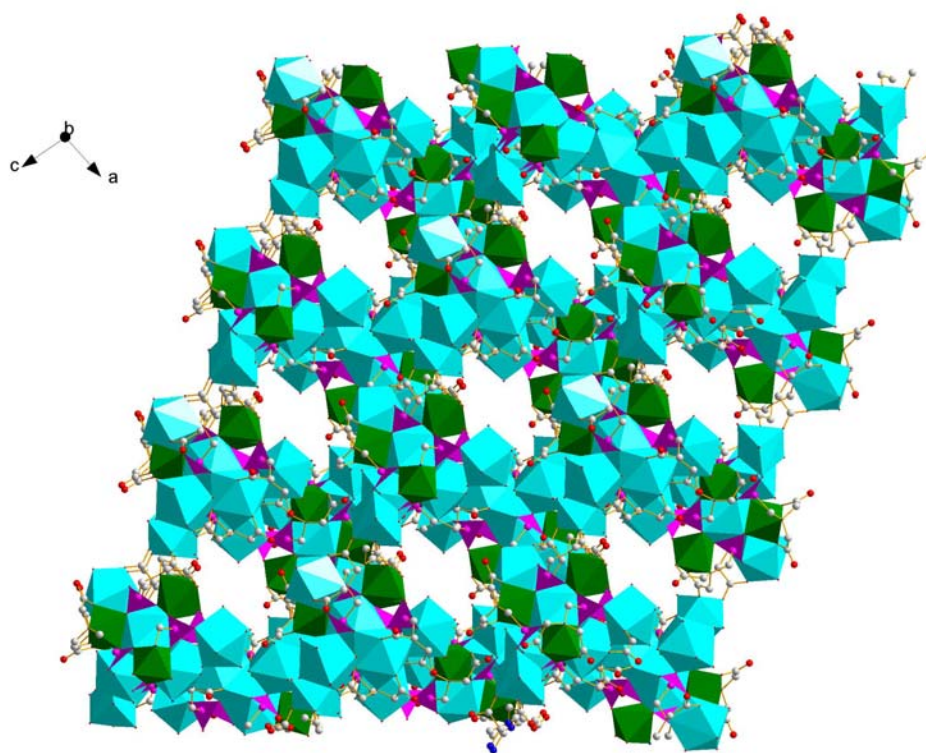


Fig. S3 Polyhedron plot of the 3D structure of **1**. The guest water molecules in the channel were omitted for clarity.

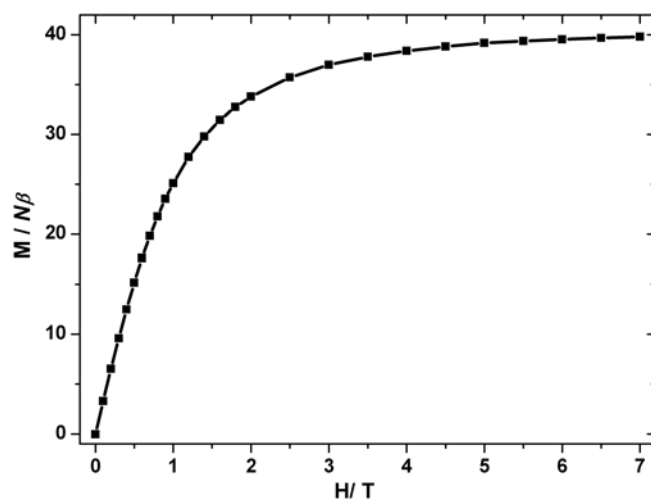


Fig. S4 Field dependence of the magnetization (M) of complex **1** at 2 K.

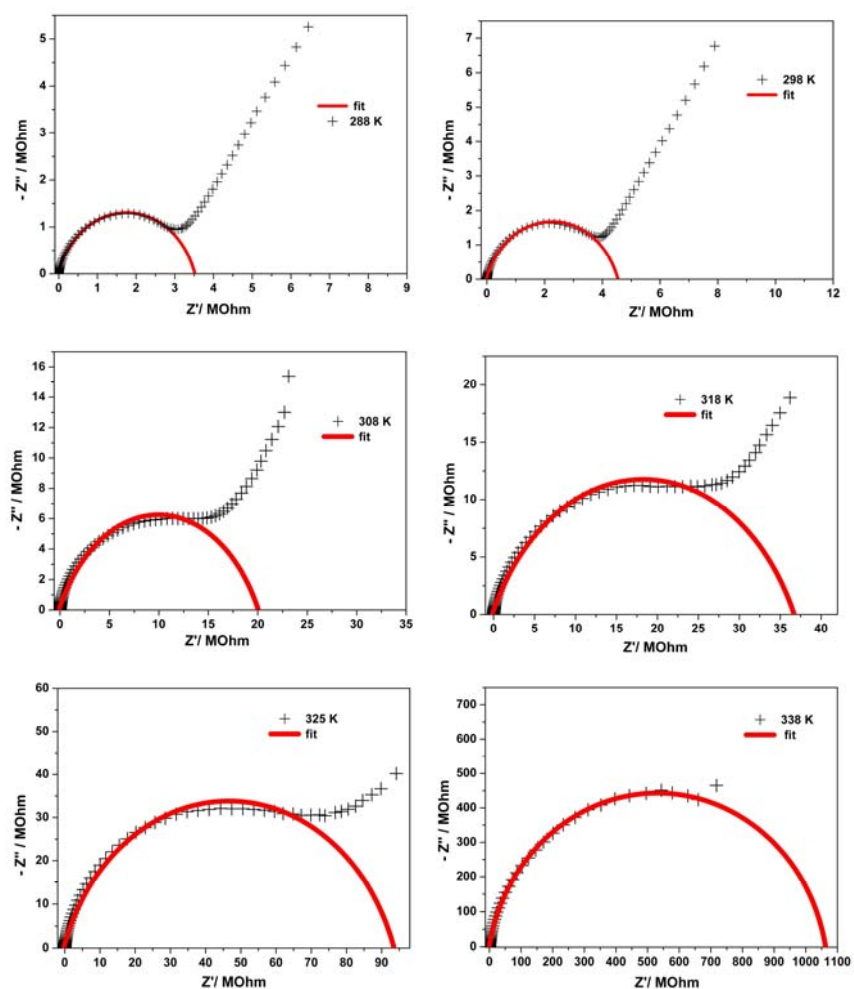


Fig. S5. Plots of temperature-dependence AC impedance for powder sample of **1** with the experiment data (donated +) and theory data (red solid line).

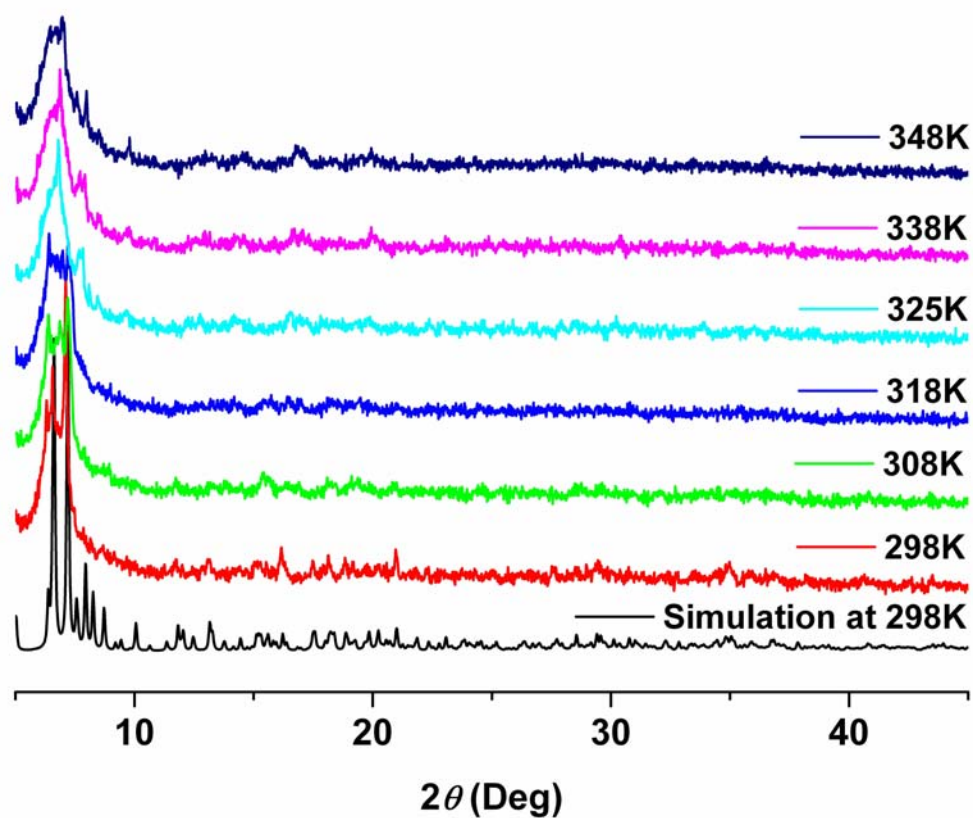


Fig. S6. PXRD plots of **1** at different temperatures, shown together with the corresponding simulation according to single crystal structural determinations.