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Monometallic Lanthanoid Assembly Showing Ferromagnetism with a Curie Temperature of 11 K

Koji Nakabayashi and Shin-ichi Ohkoshi*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,
Toyko 113-0033, Japan

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We prepared a three-dimensional monometallic lanthanoid assembly, $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$ (THB = 1,2,4,5-tetrahydroxybenzene), that exhibits ferromagnetism with a Curie temperature of 11 K. Such a ferromagnetic ordering is due to the effective mediation of the magnetic interaction between Ho^{3+} ions by the THB^{4-} ligand.

Lanthanoid metals are attractive as magnetic materials because of their high spin numbers and strong magnetic anisotropies on the 4f orbitals.[1] Magnetic materials based on lanthanoid metal or lanthanoid metal oxides have extensive applications.[1] In contrast, most metal assemblies based on lanthanoid complexes do not show ferromagnetic ordering because of the weak magnetic interaction between magnetic ions.[2] Hence, observation of ferromagnetism on metal assemblies containing lanthanoid complexes has been limited to a few bimetallic assemblies (3d−4f or 5d−4f system), e.g., $TbCr(CN)_6$, $SmFe(CN)_6$, $Sm_xGd_{1-x}[Cr(CN)_6]$, $Sm(H_2O)_5[W(CN)_8]$, and $[Co_2Gd(2,6\text{-diacetoacetylpyridine})_2(H_2O)_4][Cr(CN)_6]$.[3] Although there are paramagnetic compounds showing magnetic interactions between lanthanoid ions, a spontaneous magnetization in monometallic lanthanoid metal assemblies has yet to be reported.[4] In this work, we synthesized a three-dimensional (3-D) monometallic assembly composed of Ho^{3+} ions and 1,2,4,5-tetrahydroxybenzene (THB), $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$. This compound displays ferromagnetic ordering because of the Ho^{3+} magnetic moments with a Curie temperature (T_C) of 11 K and a coercive field (H_C) of 170 Oe. The present ferromagnetism is due to the effective mediation of magnetic interactions between Ho^{3+} ions by the π orbitals of THB^{4-}. To our knowledge, this is the first example of a monometallic lanthanoid metal assembly exhibiting a spontaneous magnetization.

The ligand, THB, was prepared according to the literature.[5] Under argon, a 1 M THB aqueous solution was mixed

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*To whom correspondence should be addressed. E-mail: ohkoshi@chem.s.u-tokyo.ac.jp.

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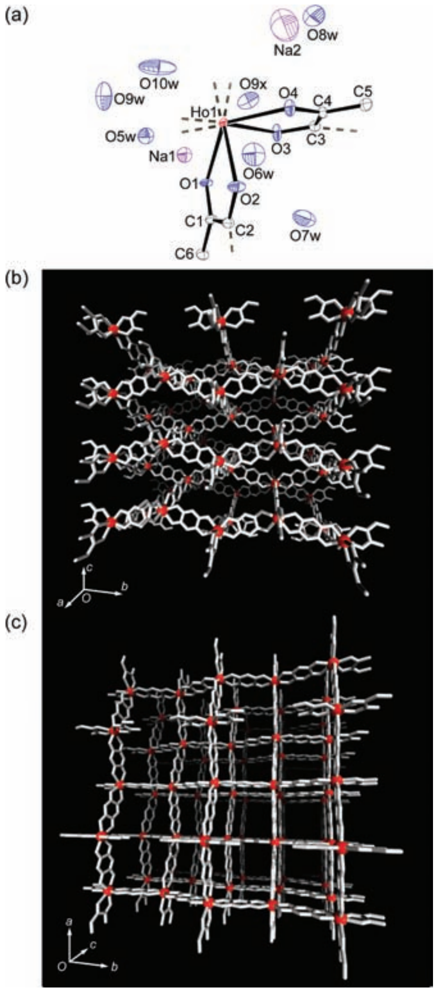
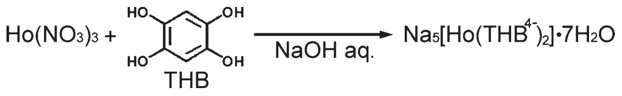


Figure 1. (a) Thermal ellipsoid plots (50% probability level) of the molecular structure of $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$. All independent atoms, including water and Na^+ ions, are labeled. H atoms are omitted for clarity. Red, purple, blue, and light gray represent Ho, Na, O, and C atoms, respectively. (b) X-ray crystal structure along the *a* axis. Red and light gray represent Ho and other atoms (C and O), respectively. (c) X-ray crystal structure along the channel direction, the *c* axis. Water molecules, Na^+ ions, and H atoms are omitted for clarity.

Scheme 1



with a 0.1 M $Ho(NO_3)_3$ aqueous solution. Slow complexation of the mixed solution in a 2.5 M NaOH aqueous solution for 1 week produced greenish-black single crystals of $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$ in 75% yield (Scheme 1). Elemental analysis indicated that the formula was $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$. Calcd: Ho, 23.90; C, 20.88; H, 2.63. Found: Ho, 23.52; C, 20.70; H, 2.59. N was not present. The IR spectra had C=C stretching peaks for THB at 1218 and 1459 cm^{-1}.

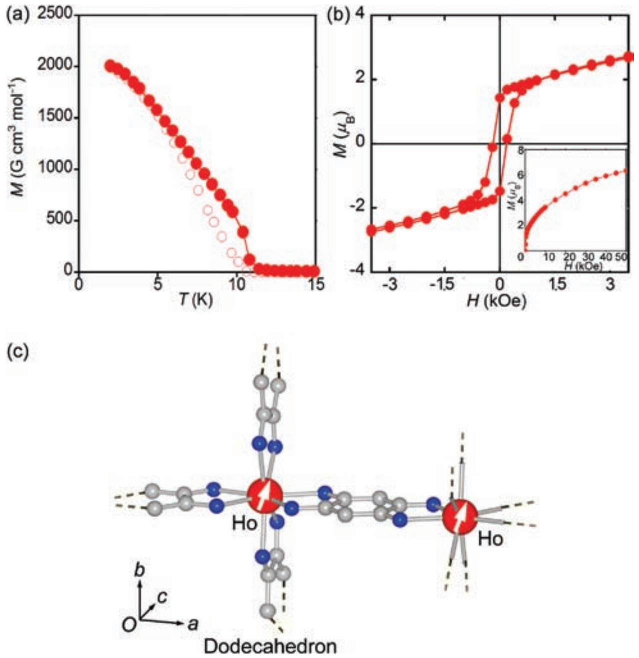


Figure 2. Magnetic properties of $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$. (a) FCM obtained with decreasing temperature in an applied field of 10 Oe (red filled circles). RM obtained with increasing temperature without an applied field after the temperature was initially lowered in an applied magnetic field of 10 Oe. (b) *M-H* hysteresis loop. Inset shows the magnetic field dependence of magnetization at 2 K. (c) Schematic illustration of magnetic ordering. Red, blue, and light gray represent Ho, O, and C atoms, respectively.

X-ray crystallographic analysis was performed using a Rigaku R-AXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation at 93 K. This compound consisted of a 3-D network (orthorhombic, *Imma*, $a = 16.700(2)$ Å, $b = 16.711(2)$ Å, $c = 9.791(1)$ Å, and $Z = 4$; Figure 1).[6] The asymmetric unit consisted of a quarter of a Ho^{3+} ion, half of a THB^{4-} anion, one-and-a-quarter Na^+ cations, and four-and-a-quarter water molecules (Figure 1a). The coordination geometry of a Ho^{3+} ion was dodecahedron (D_{4d}), where a Ho^{3+} ion was coordinated to eight O atoms from four bidentate ligands of THB^{4-}. The Ho^{3+} ion was connected via four ligands directed toward the *a* and *b* axes, which resulted in a 3-D network framework with a regulated square-grid channel (Figure 1b,c). This channel (4.9 × 4.9 Å) was occupied by Na^+ ions and noncoordinated water molecules. The Ho−Ho distances are 8.73 and 8.68 Å along the *a* and *b* axes, respectively.

The product of the molar magnetic susceptibility (χ_M) and temperature (*T*), $\chi_M T$, at room temperature was 14.4 cm^3 K mol^{-1}. This $\chi_M T$ value nearly corresponds to the predicted value of 13.9 cm^3 K mol^{-1} for Ho^{3+} ($J = 8$, $L = 6$, $S = 2$, and $g = {}^5/_4$). The field-cooled magnetization (FCM) obtained with decreasing temperature in an applied field of 10 Oe and remnant magnetization (RM) obtained with increasing temperature without an applied field after the temperature was initially lowered in an applied magnetic field of 10 Oe showed that spontaneous magnetization appeared at $T_C = 11$ K (Figure 2a). The *M* versus external magnetic field (*H*) plots at 2 K indicated that H_C was 170 Oe and the magnetization (*M*) value at 50 kOe was 6.4 μ_B (Figure 2b).

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[6] Crystal data for $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$: $C_{12}H_4O_{25}Na_5Ho$, $M = 828.03$, orthorhombic, *Imma*, $a = 16.700(2)$ Å, $b = 16.711(2)$ Å, $c = 9.791(1)$ Å, $V = 2732.2(5)$ Å^3, $Z = 4$, $T = 93$ K, $D_c = 2.013$ g cm^{-3}, λ(Mo Kα) = 0.710 73 Å, 12 643 reflections measured, 1680 unique ($R_{int} = 0.067$), which were used in all calculations. All calculations were performed using the *CrystalStructure* crystallographic software package. The structure was solved by a direct method (*SHELXL-97*) and refined by full-matrix least-squares methods on F^2 with 134 parameters. R1 = 0.0568 [$I > 2\sigma(I)$] and wR2 = 0.1527, GOF = 1.160; max/min residual density = 1.89/−2.98 e Å^{-3}. Details of the refinement are described in a CIF file.

The observed M value of 6.4 μ_B at 2 K in 5 T is close to the expected value of 6.8 μ_B, which suggests that the sublevels of $|+5\rangle$ and $|-5\rangle$ are the lowest energy levels and are populated at a very low temperature.[2k,7]

To our knowledge, this is the first example of a monometallic lanthanoid complex displaying a ferromagnetic phase transition. The ferromagnetic ordering is due to the effective mediation of the magnetic interactions between Ho^{3+} ions by the π orbitals of THB^{4-}.[8] Using this ligand, a variety of monometallic lanthanoid metal assemblies may be synthesized. In addition, mixing lanthanoid metal ions (e.g., $Sm_xHo_{1-x}(THB^{4-})_2$), which should show a new magnetic function, is possible. A study to clarify these hypotheses is currently underway.

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Supporting Information Available: X-ray crystal structure and crystallographic data of $Na_5[Ho(THB^{4-})_2]\cdot 7H_2O$, $\chi T-T$ plots, and estimation of J_{Ho-Ho} based on a Heisenberg model, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 721332, which contains the supplementary crystallographic data for this paper, can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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