One-dimensional Structure Consisting of Pin-wheel Cu_4Gd Core and Na^+ as Connector

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A 3d–4f complex with the formula of $\{Na[(CuL)_4Gd]\}_{1\infty}$ was prepared, where $(CuL)^-$ is a "ligand-complex," [*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamato]copper(II). The structure consists of a pin-wheel-like Cu_4Gd core and Na^+ ion as a connector to give a one-dimensional chain. The magnetic data and their analyses demonstrated an intramolecular ferromagnetic interaction within a Cu_4Gd core and an intercore antiferromagnetic interaction operating through Na^+ ion with the coupling parameters of $J = +1.09\,cm^{-1}$, $zJ' = -0.07\,cm^{-1}$; $S_{Cu} = 1/2$, $S_{Gd} = 7/2$).

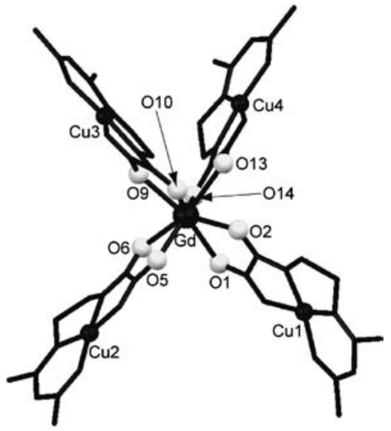

Figure 1. Molecular structure of a pin-wheel-like $\{(CuL)_4Gd\}^-$ core. Dihedral angle between adjacent Cu^{2+} coordination planes: 61.2° (Cu1–Cu2), 106.1° (Cu2–Cu3), 70.2° (Cu3–Cu4), and 119.9° (Cu4–Cu1).

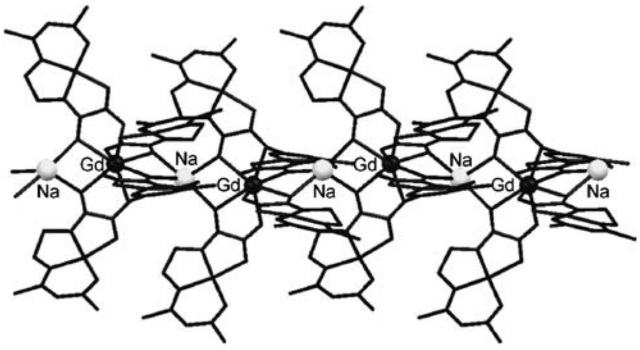

Figure 2. 1D structure of $Na[(CuL)_4Gd]$ consisting of alternately arrayed pin-wheel-like Cu_4Gd core and Na^+ ion as a connector along the chain.

The discovery of single-molecule magnets (SMMs) in Mn_{12} cluster and the subsequent extensive development are ones of the most important achievements of molecular magnetism, because the slow relaxation of SMMs provides the properties such as molecular magnetic hysteresis and quantum tunneling of the magnetization.[1] In principle, slow relaxation of the magnetization can also be expected in one-dimensional (1D) materials, as suggested by Glauber,[2] and single-chain magnets (SCMs) have been found in several 1D materials.[3] Now SMMs and SCMs are ones of the most important compounds in the field of molecule-based magnetism. In recent years, molecular design of SMMs and SCMs containing f-block elements has attracted much attention,[4] because the molecular magnetic anisotropy, that is one of the conditions required for SMMs and SCMs, is easily derived from 4f ion such as Tb^{III} and Dy^{III} ion. In this study, in order to look for a new 3d–4f molecular system adaptable for SMMs and SCMs, a 1D complex $\{Na[(CuL)_4Gd]\}_{1\infty}$ consisting of a pin-wheel-like Cu_4Gd core and Na^+ ion as a connector has been studied. We report here the synthesis, unique 1D structure, and magnetic properties.

Complex $\{Na[(CuL)_4Gd]\}_{1\infty}$ was prepared as purple crystals by mixing $Na[CuL]\cdot1.33H_2O$ (H_3L = *N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid)[5] and $Gd(hfac)_3\cdot2H_2O$ with 1:4 molar ratio in methanol at ambient temperature.[6] The FAB mass spectrum exhibited relatively large peaks assignable to $\{Na[(CuL)_3Gd]\}^+$, suggesting that Na^+ ion bounds to the molecule.

The crystal structure of $Na[(CuL)_4Gd]$ was determined by single-crystal X-ray diffraction analyses.[7] Figure 1 shows a pentanuclear pin-wheel-like Cu_4Gd core, where the central Gd^{III} ion is coordinated by eight oxygen atoms of four "ligand-complexes." The eight Gd–O distances are Gd–O(1) = 2.408(4), Gd–O(2) = 2.403(3), Gd–O(5) = 2.360(4), Gd–O(6) = 2.446(3), Gd–O(9) = 2.361(5), Gd–O(10) = 2.424(3), Gd–O(13) = 2.408(4), and Gd–O(14) = 2.413(3) Å. Each Cu^{II} complex assumes a square-planar N_2O_2 coordination geometry and coordinates to Gd^{III} ion by two oxygen atoms at the terminal oximate site as an electrically mononegative bidentate "ligand-complex."

Figure 2 shows a 1D structure of $Na[(CuL)_4Gd]$ running along the *b* axis, where Na^+ ion plays as a connector to form a 1D structure with Gd–Gd distance of 7.493 Å and Na^+–Gd distances of 3.798 and 3.788 Å. Within the 1D chain, a Na^+ ion is bound by two oxygen atoms of two $(CuL)_2$ of a $[(CuL)_4Gd]$ core and two oxygen atoms of two $(CuL)_2$ of the adjacent Cu_4Gd core, with the Na^+–O distances in the range of 2.407(4)–2.473(4) Å. Further, the Na^+ ion is bound by a water molecule with Na^+–O = 2.347(7) Å.

The temperature dependence of the magnetic susceptibility of $Na[(CuL)_4Gd]$ was measured in the temperature range of

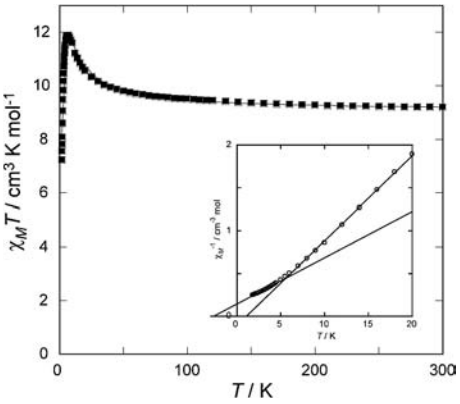

Figure 3. The temperature dependence of the magnetic susceptibility of Na[(CuL)$_4$Gd] as the plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T at the lower-temperature region in inset.

2.0–300.0 K under the external magnetic field of 0.5 T. Figure 3 shows the plots of $\chi_M T$ vs. T and those of $1/\chi_M$ vs. T in inset, where χ_M is the molar magnetic susceptibility per Cu$_4$Gd corrected by diamgnetism and temperature-independent paramagnetism of Cu^{2+}. The $\chi_M T$ value of 9.20 cm^3 K mol^{-1} at 300.0 K is compatible with the theoretical value of 9.375 cm^3 K mol^{-1} calculated for non-interacting four Cu^{II} ($S = 1/2$) and one Gd^{III} ($4f^7, J = 7/2, L = 0, S = 7/2, {}^8S_{7/2}$) non-interacting ions.[8] On lowering the temperature, the $\chi_M T$ value increases gradually to reach a maximum value of 11.89 cm^3 K mol^{-1} at 6.0 K and then abruptly decreases to 7.80 cm^3 K mol^{-1} at 2.0 K. The increase in the higher-temperature region indicates the operation of an intramolecular ferromagnetic interaction between Cu^{II} and Gd^{III} ions, while the decrease in the lower-temperature region can be ascribed to intermolecular antiferromagnetic interaction. As shown in inset of Figure 3, the reciprocal magnetic susceptibility in the higher-temperature range of 50–300 K follows the Curie–Weiss equation of $1/\chi_M = (T - \theta)/C$ with Curie constant of $C = 9.11$ cm^3 K mol^{-1} and positive Weiss constant of $\theta = +3.7$ K. The reciprocal magnetic susceptibility in the lower-temperature range below 5 K follows the Curie–Weiss equation of $1/\chi_M = (T - \theta)/C$ with negative Weiss constant of $\theta = -2.6$ K. The result from the $1/\chi_M$ vs. T plots is consistent with the coexistence of a ferromagnetic and an antiferromagnetic interaction. The magnetic susceptibility can be reproduced by the equation derived from the spin-only Hamiltonian based on the pentanuclear pin-wheel-like Cu$_4$Gd structure, $H = \beta H(4g_{\text{Cu}}S_{\text{Cu}} + g_{\text{Gd}}S_{\text{Gd}}) - 2JS_{\text{Gd}}(S_{\text{Cu1}} + S_{\text{Cu2}} + S_{\text{Cu3}} + S_{\text{Cu4}})$, since the ground state of the Gd^{III} ion (${}^8S_{7/2}$) has no contribution from orbital angular momentum. The solid line in Figure 3 shows the calculated curve with the parameters of $g_{\text{Gd}} = 2.00$(fixed), $g_{\text{Cu}} = 2.11$, $J = +1.09$ cm^{-1}, $zJ' = -0.07$ cm^{-1}, and 0.4% of mononuclear Cu^{II} impurity, demonstrating that both ferromagnetic intramolecular interaction within Cu$_4$Gd core and antiferromagnetic intermolecular interaction are essential for the fitting.

The field dependence of the magnetization at 2.0 K upto 5 T was measured. The plots in the form of $M/N\beta$ vs. H were compared with the Brillouin functions calculated for possible spin states for Cu$_4$Gd ($S_{\text{Cu}} = 1/2$, $S_{\text{Gd}} = 7/2$). The experimental curve is lower than the calculated curve of the possible highest spin ground state $S = 11/2$ resulting from the intramolecular ferromagnetic coupling within the molecule of Cu$_4$Gd and higher than the curve of magnetically independent four $S_{\text{Cu}} = 1/2$ and one $S_{\text{Gd}} = 7/2$. The temperature- and field-dependent magnetic data both suggest a intracore ferromagnetic interaction and a relatively strong intermolecular antiferromagnetic interaction mainly operating through Na$^+$ ion.

In conclusion, we have reported a 1D complex $\{\text{Na}[(\text{CuL})_4\text{Gd}]\}_{1\infty}$ consisting of a pin-wheel-like Cu$_4$Gd core and Na$^+$ ion as a connector and exhibiting intracore ferromagnetic interaction and intercore antiferromagnetic interaction. When the intercore magnetic interaction was tuned by the use of a proper connector and the central Gd^{III} ion was replaced by anisotropic magnetic Ln^{III} ion, the resulted compound can be a good candidate for either a SMMs or SCMs. The study along this line is now in progress.

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References and Notes

1 a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Noval, *Nature* **1993**, *365*, 141. b) G. Christou, *Polyhedron* **2005**, *24*, 2065. c) D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054.

2 R. J. Glauber, *J. Math. Phys.* **1963**, *284*, 133.

3 a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem., Int. Ed.* **2001**, *40*, 1760. b) R. Clerac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837.

4 a) N. Ishikawa, M. Sugita, W. Wernsdorfer, *J. Am. Chem. Soc.* **2005**, *127*, 3650. b) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, *J. Am. Chem. Soc.* **2004**, *126*, 420. c) A. Mishra, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 15648. d) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. Pecoraro, *Angew. Chem., Int. Ed.* **2004**, *43*, 3912. e) J.-P. Costes, F. Dahan, W. Wernsdorfer, *Inorg. Chem.* **2006**, *45*, 5. f) F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, *J. Am. Chem. Soc.* **2006**, *128*, 1440.

5 A "ligand-complex," Na[CuL]$\cdot$1.33H$_2$O, was prepared according to the literature. J.-P. Costes, F. Dahan, J.-P. Laurent, *J. Chem. Soc., Dalton Trans.* **1989**, 1017.

6 Na[(CuL)$_4$Gd]: A methanolic solution (30 mL) of Na[CuL]$\cdot$1.33H$_2$O (0.13 g, 0.4 mmol) was gently poured into a methanolic solution (10 mL) of Gd(hfac)$_3$(H$_2$O)$_2$ (0.81 g, 0.1 mmol) at ambient temperature. The resulting solution was allowed to stand for several days, during which time blue-purple crystals precipitated, and they are collected by suction filtration. Crystals easily loose the crystal solvents, and the elemental analysis agrees with the formula of Na[(CuL)$_4$Gd]. Yield: 0.09 g (67%). IR (cm^{-1}): $\nu_{\text{C=O}}$ 1655; $\nu_{\text{C=N}}$ 1596. Anal. Calcd for C$_{36}$H$_{44}$N$_8$O$_{16}$NaCu$_4$Gd: C, 33.80; H, 3.47; N, 8.76%. Found: C, 33.85; H, 3.62; N, 9.04%.

7 A crystal with a small amount of mother liquid was encapsulated into a glass tube, and the X-ray diffraction data were collected. Crystal data for Na[(CuL)$_4$Gd]$\cdot$3H$_2$O$\cdot$2MeOH: formula C$_{38}$H$_{58}$N$_8$O$_{21}$NaCu$_4$Gd, $M_r = 1397.34$, monoclinic, space group $P2_1/c$, $a = 14.035(3)$, $b = 14.766(3)$, $c = 26.088(6)$ Å, $\beta = 94.59(1)°$, $V = 5389(2)$ Å^3, $Z = 4$; $d_{\text{calcd}} = 1.722$ Mg/m^3; $\mu = 2.857$ mm^{-1}; $T = 296$ K; $R = 0.0451$, $wR = 0.1242$. Crystallographic data deposit number CCDC 663223.

8 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.