Chiral Ferromagnetic Chain of Copper(II)–Gadolinium(III) Complex

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A chiral one-dimensional copper(II)–gadolinium(III) complex $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$ ($H_3L^{dpen(1S2S)}$ = (1*S*,2*S*)-1,2-diphenyl-1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane, Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) was synthesized, where Cu^{II} and Gd^{III} ions are alternately arrayed to form a ferromagnetic chain.

Since the discovery of single molecule magnets (SMMs) in Mn_{12} clusters,[1] a number of SMMs and single chain magnets (SCMs)[2] of polynuclear transition-metal complexes have been synthesized. More recently, SMMs and SCMs of polynuclear 3d–4f complexes have attracted much attention.[3] In a previous paper, we reported the first 3d–4f SMM,[4a] $[Cu^{II}LTb^{III}(hfac)_2]_2$, derived from the assembly of $K[Cu^{II}L]$ and $[Tb^{III}(hfac)_3(H_2O)_2]$, where H_3L = 1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethylene and Hhfac = hexafluoroacetylacetone). In the assembly, $[Cu^{II}L]^-$ and $[Tb^{III}(hfac)_3(H_2O)_2]$ function as donor and acceptor components, respectively. The assembled compound $[Cu^{II}LTb^{III}(hfac)_2]_2$ has a cyclic tetranuclear $[Cu^{II}_2Tb^{III}_2]$ structure assuming a center of symmetry. In this study, a chiral component of $Na[Cu^{II}L^{dpen(1S2S)}]\cdot 3CH_3CN$ ($H_3L^{dpen(1S2S)}$ = (1*S*,2*S*)-1,2-diphenyl-1-(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane), instead of $K[Cu^{II}L]$, was used for the assembly reaction, in the hope that a different assembly structure can be generated. As anticipated, a chiral ferromagnetic chain structure of the Cu^{II}–Gd^{III} complex $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$, that is definitely different from the cyclic tetranuclear structure, was obtained. We report the structure and the magnetic properties.

Asymmetrical ligand $H_3L^{dpen(1S2S)}$ was prepared by a 1:1:1 condensation reaction of phenylsalicylate, (1*S*,2*S*)-diphenylethanediamine, and *o*-vanillin. The Cu^{II} complex was synthesized by the reaction of the ligand, copper(II) acetate monohydrate, and sodium methoxide in 1:1:3 molar ratio in methanol. The crude product was recrystallized from acetonitrile to give the precursor complex $Na[Cu^{II}L^{dpen(1S2S)}]\cdot 3CH_3CN$ as deep red block crystals. The assembly reaction of $Na[Cu^{II}L^{dpen(1S2S)}]\cdot 3CH_3CN$ and $[Gd^{III}(thd)_3]$ (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) gave crystals of $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$.[5] A crystal coated by Nujol was used for X-ray diffraction analysis.[6] The complex crystallized into a chiral space group $P3_221$ (No. 154). The one-dimensional (1-D) structure with the relevant atom numbering is shown in Figure 1, where the crystallographic unique unit consists of two molecular units. Each Cu^{II} ion has a square-planar coordination geometry with N_2O_2 donor atoms of the asymmetrical tetradentate ligand. The Cu^{II} complex functions as "bridging ligand-complex" to the two Gd^{III} ions. The two phenoxo and the methoxy oxygen atoms at one side of the planar Cu^{II} complex coordinate to a Gd^{III} ion as a tridentate ligand. The amido oxygen atom on the opposite side of the Cu^{II} complex coordinates to another Gd^{III} ion as a monodentate ligand. Including the coordination of the two thd^- ions as a didentate chelate ligand, the Gd^{III} ion has an octacoordinate geometry with the O_8 oxygen atoms.

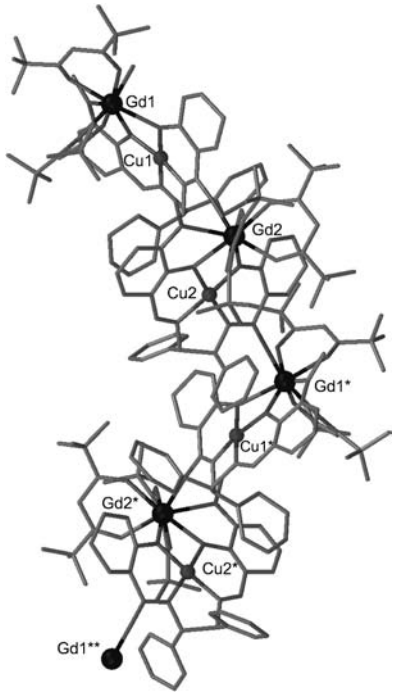

Figure 1. 1-D chain structure of $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$ along the *b* axis. The Cu^{II} and Gd^{III} ions are alternately arrayed.

A chiral 1-D structure runs along the *b* axis, in which Cu^{II} and Gd^{III} ions are alternately arrayed. Within a chain, one Cu^{II}–Gd^{III} is linked by the phenoxy oxygen and another Cu^{II}–Gd^{III} is linked by the amido group.

The temperature dependence of the magnetic susceptibilities was measured in the temperature range of 2.0–300.0 K under an external magnetic field of 0.5 T. Figure 2 shows the plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T, where χ_M is the molar magnetic susceptibility per $Cu^{II}Gd^{III}$. The plots of $1/\chi_M$ vs. T in the temperature range of 50–300 K follow the Curie–Weiss equation ($1/\chi_M = (T-\theta)/C$) with $C = 7.9\,cm^3\,K\,mol^{-1}$ and the $\theta = +8.8$ K, demonstrating an intrachain ferromagnetic interaction. The $\chi_M T$ value of $8.14\,cm^3\,K\,mol^{-1}$ at 300 K is compatible with the calculated value of $8.25\,cm^3\,K\,mol^{-1}$ expected for magnetically isolated one Cu^{II} ($S = 1/2$) and one Gd^{III} ($4f^7$, $J = 7/2$, $L = 0$, $S = 7/2$, $^8S_{7/2}$) ions with $g = 2.00$. On lowering the temperature, the $\chi_M T$ value increases to reach a maximum value of

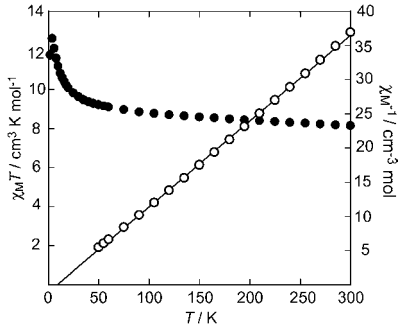

Figure 2. The plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T, where χ_M is the molar magnetic susceptibility per CuGd. The plots of $1/\chi_M$ vs. T in the temperature range of 50–300 K follow the Curie–Weiss equation ($1/\chi_M = (T - \theta)/C$) with $C = 7.9\,\mathrm{cm^3\,K\,mol^{-1}}$ and the $\theta = +8.8\,\mathrm{K}$.

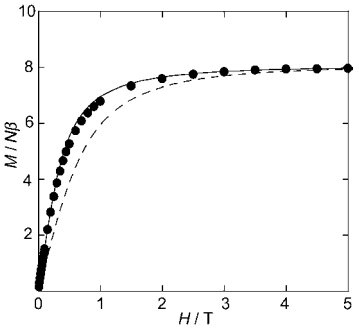

Figure 3. The field dependence of the magnetization per CuGd up to 5 T at 2.0 K, as the plots of $M/N\beta$ vs. H. The calculated curves of $M/N\beta$ vs. H with the Brillouin functions of $S = 8 \times 1/2$ ($(Cu^{II}–Gd^{III}–Cu^{II}–Gd^{III})/2$) and $S = 4(Cu^{II}–Gd^{III})$ are drawn in the solid and broken lines, respectively.

$12.59\,\mathrm{cm^3\,K\,mol^{-1}}$ at 4.0 K, and then decreases. The increase of $\chi_M T$ vs. T plot in the higher temperature region indicates the operation of an intrachain ferromagnetic interaction between Cu^{II} and Gd^{III} ions. The χ_M value increases on lowering the temperature over the whole temperature region, suggesting no or very weak magnetic interchain interaction. The field dependence of the magnetization up to 5 T at 2.0 K is shown in Figure 3, as the plots of $M/N\beta$ vs. H. The experimental data per CuGd is much higher than the calculated curve of Brillouin function of $S = 4$ (broken line in Figure 3), where spin state of $S = 4$ is expected for a ferromagnetic coupled Cu^{II}–Gd^{III} species. The data is rather close to the theoretical curve of $S = 8 \times 1/2$, whose spin ground states (solid line) can be resulted from the ferromagnetic coupling of Cu^{II}–Gd^{III}–Cu^{II}–Gd^{III}. The magnetization and the magnetic susceptibility data demonstrate that 1-D complex $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$ is a ferromagnetic chain.

In this study, we have reported a chiral 1-D ferromagnetic chain of a Cu^{II}–Gd^{III} complex derived from the assembly of Na-$[Cu^{II}L^{dpen(1S2S)}]\cdot 3CH_3CN$ and $[Gd^{III}(thd)_3]$. In the assembly, the former complex functions as a chiral donor species in the formation of coordination bonds and the latter complex functions as an acceptor species. In addition to the introduction of chirality, steric repulsion from the two latelal phenyl groups of $[Cu^{II}L^{dpen(1S2S)}]^-$ and the bulkier thd^- might be an important factor for adopting 1-D sturucture. In our previous studies, we showed that the assembly of an achiral species of $K[Cu^{II}L]$ and $[Gd^{III}(hfac)_3(H_2O)_2]$ gave a cyclic tetranuclear structure assuming a center of symmetry.[4] These two results demonstrate that the introduction of the chirality into the assembly reaction brought a definitely different assembly structure, that is, 1-D chain, instead of cyclic structure. The present result showed that introduction of chiralty to molecular design is an important factor to govern the assembly structure. We are now studying on the SMMs and SCMs properties for the analogous d–f complexes.

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5 $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$: A solution of $Na[CuL^{dpen(1S2S)}]\cdot 3CH_3CN$ (0.300 mg, 0.5 mmol) in 20 mL of chloroform was added to a solution of $[Gd(thd)_3]$ (0.350 mg, 0.5 mmol) in 20 mL of chloroform, and the mixed solution was warmed for 1 h. The resulting solution was evaporated to dryness. The crude product was dissolved in methanol and filtered. The filtrate was allowed to stand for several days, during which time orange square block crystals precipitated. Yield: 0.30 g (59%). Anal. Calcd for $C_{51}H_{61}N_2O_8CuGd$: C, 58.29; H, 5.85; N 2.66%. Found: C, 58.29; H, 6.07; N, 2.68%.

6 X-ray crystallographic data for $[Cu^{II}L^{dpen(1S2S)}Gd^{III}(thd)_2]_n$ at 296 K: Due to the poor quality of the X-ray data, the crystal solvent molecules and a part of the thd ligands were not clearly determined. formula $C_{51}H_{61}N_2O_8CuGd$, fw 1048.83, trigonal, space group $P3_221$ (No. 154), $a = b = 25.262(6)$ Å, $c = 32.106(11)$ Å, $V = 17745(9)$ Å^3, $Z = 12$, $D_{calcd} = 1.178\,\mathrm{g\,cm^{-3}}$; $\mu = 1.518\,\mathrm{mm^{-1}}$; $R = 0.0944$, $wR = 0.141$, Flack parameter = 0.10(3). The crystallographic data can be obtained free of charge via Internet from the Cambridge Crystallograhic Data Centre. Data (CCDC 733874).

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