

## Stepwise Synthesis and Magnetic Control of Trimetallic Magnets [Co<sub>2</sub>Ln(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Cr(CN)<sub>6</sub>] $\cdot$ *n*H<sub>2</sub>O (Ln = La, Gd; H<sub>2</sub>L = 2,6-Di(acetoacetyl)pyridine) with 3-D Pillared-Layer Structure

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In the last few decades, coordination compounds which provide diversified and tunable frameworks or electric structures, play a key role in the field of functional materials.<sup>1–8</sup> The construction of desired assembled structures and the control of their physical properties can be achieved by integrating appropriate constituents with sophisticated designs. Recently, much attention has been devoted to quantum effects<sup>4</sup> and the multifunction of molecule-based magnets in this area.<sup>5</sup> Lanthanide (4f metal) ions are promising components of functional materials because of their large magnetic anisotropy arising from the strong L-S coupling and fluorescent characteristics. However, 4f metal ions were not often used as a constituent of molecule-based magnets because magnetic interaction in 4f-metal condensed systems is generally weak.<sup>6</sup> Some magnetic compounds comprising 3d and 4f metal ions have been prepared, but their magnetic phase transition temperature remains low because of the weak magnetic interaction between 3d and 4f ions: the highest *T<sub>c</sub>* of 11.7 K has been reported for Prussian-blue analogue Tb[Cr(CN)<sub>6</sub>] $\cdot$ 4H<sub>2</sub>O.<sup>7</sup> Apart from the *T<sub>c</sub>*, the insertion of a 4f metal ion into a 3d metal ion(s) magnetic network is important for developing new multifunctional molecule-based magnets. Several 1-D and 2-D 3d–3d–4f trimetallic assemblies have been reported; however, they showed no magnetic ordering because of low dimensionality.<sup>8</sup> Here we report two novel 3-D trimetallic molecule-based magnets developed by stepwise aggregation of trinuclear Co(II)<sub>2</sub>Ln(III) complexes (Ln = La and Gd) and [Cr(CN)<sub>6</sub>]<sup>3–</sup> and describe the effects of the diamagnetic La(III) and paramagnetic Gd(III) ions on their magnetic properties.

Linear trinuclear Co(II)Ln(III)Co(II) complexes, [Co<sub>2</sub>Ln(L)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] $\cdot$ 4H<sub>2</sub>O (Ln = La (**1**) and Gd (**2**); H<sub>2</sub>L = 2,6-di(acetoacetyl)pyridine), were prepared by the method in our previous papers (Figures S1–S3 in Supporting Information).<sup>9</sup> They were mixed with K<sub>3</sub>[Cr(CN)<sub>6</sub>] in 1:1 molar ratio in an aqueous solution to give [Co<sub>2</sub>Ln(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Cr(CN)<sub>6</sub>] $\cdot$ *n*H<sub>2</sub>O ((Ln, *n*) = (La, 3; **3**) and (Gd, 2; **4**)) as reddish-orange crystals.<sup>10</sup> Single-crystal X-ray crystallography for each complex reveals the formation of a 3-D pillared-layer structure, and they are isomorphous.<sup>11</sup> The asymmetric unit consists of two crystallographically independent [Co<sub>2</sub>Ln(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup> and two [Cr(CN)<sub>6</sub>]<sup>3–</sup> units (Figure 1). The trinuclear units have a linear Co(II)Ln(III)Co(II) core held by four enolate-bridges between two L<sup>2–</sup> ligands. Each Co(II) ion is located at  $\beta$ -diketone sites of L<sup>2–</sup> and has an elongated octahedral geometry together with two axial cyano nitrogen atoms. The Ln(III) ion in the 2,6-diacetylpyridine site has a ten-coordinate geometry with four water molecules above and below the {Co<sub>2</sub>Ln(L)<sub>2</sub>} plane.

Four equatorial cyano groups of [Cr(CN)<sub>6</sub>]<sup>3–</sup> coordinate to adjacent Co(II) ions to form a 2-D grid layer extended by Cr–

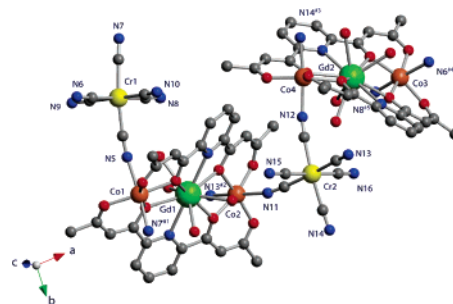


Figure 1. The asymmetric unit of [Co<sub>2</sub>Gd(L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Cr(CN)<sub>6</sub>] $\cdot$ 2H<sub>2</sub>O (**4**).<sup>12</sup>

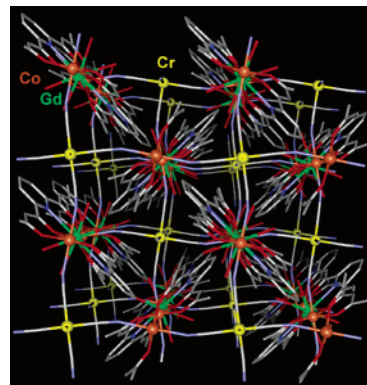


Figure 2. Projection of the 3-D network of **4** along the *c*-axis. Atoms: Co (Orange), Gd (Green), Cr (Yellow), N (blue), O (red), C (gray).

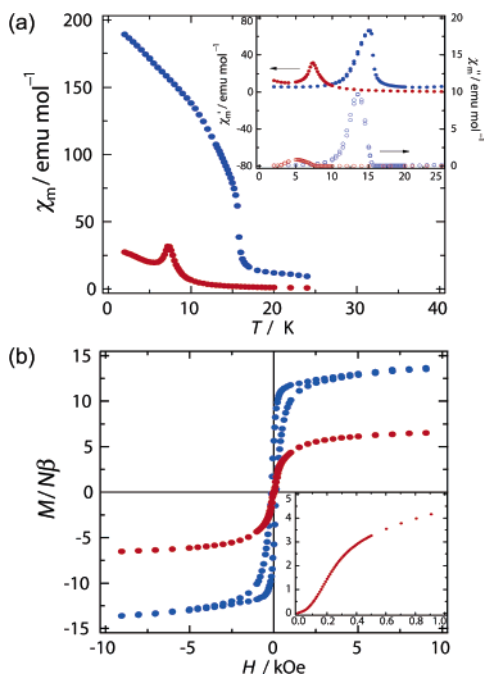
CN–Co linkages on the *ab* plane (Figure 2). In the lattice, there are two kinds of 2-D layer; one is extended by Cr(1)–CN–Co(1 and 3) linkages and the other is extended by Cr(2)–CN–Co(2 and 4) ones. The trinuclear {Co<sub>2</sub>Ln(L)<sub>2</sub>} moieties are perpendicularly located to the 2-D layers and the two Co(II) ions in the same trinuclear unit are each involved in different layers. As the result, two kinds of 2-D layer are alternately aligned along the *c*-axis and spliced by the {Co<sub>2</sub>Ln(L)<sub>2</sub>} trinuclear pillar units affording a 3-D framework. The {Co<sub>2</sub>Ln(L)<sub>2</sub>} moiety is not planar and the two ligands show a significant twist with respect to the central Ln(III) ion: the two {LnONO} least-square planes defined by Ln and {ONO} of each L<sup>2–</sup> are twisted with a dihedral angle of 25.56° for **3** and 27.73° for **4**. Also the two {CoO<sub>4</sub>} planes in the trinuclear unit are not coplanar owing to the twisting. The average dihedral angle between the two least-squares {CoO<sub>4</sub>} planes is 31.68° for **3** and is 29.56° for **4**. The next layer shifts toward 0.5 cycle of each *a*-, *b*-, and *c*-axis from the original topology because of the twisted trinuclear pillar units.

The magnetic behavior of **4** with paramagnetic Gd(III) ion is shown in Figures 3 and S5. The  $\chi_m T$  value at room-temperature per Co(II)<sub>2</sub>Gd(III)–Cr(III) unit is 16.97 emu mol<sup>–1</sup> K (11.65  $\mu_B$ ).

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**Figure 3.** (a) Field-cooled-magnetization (FCM) curve for **3** (red dot) and **4** (blue dot) under a dc field of 5 Oe. The inset shows  $\chi_m'$  (closed circle) and  $\chi_m''$  (open circle) vs  $T$  plots for **3** (red) and **4** (blue) under an ac field of 3 Oe. (b) Magnetic hysteresis loops for **3** (red dot) and **4** (blue dot). The inset is the first magnetization curve for **3**.

This value is close to the algebraic summations of the magnetic susceptibilities of complex **2** and  $K_3[\text{Cr}(\text{CN})_6]$  ( $15.99 \text{ emu mol}^{-1} \text{ K}$ ). The  $\chi_m T$  value gradually increased with decreasing temperature to the maximum value of  $678.7 \text{ emu mol}^{-1} \text{ K}$  at 12 K and then rapidly decreased down to  $166.1 \text{ emu mol}^{-1} \text{ K}$  at 2 K. The abrupt increase in  $\chi_m T$  around 12 K suggests an onset of three-dimensional ferromagnetic ordering. Temperature-dependences of the ac magnetic susceptibility are shown in Figure 3a (inset). Both in-phase ( $\chi_m'$ ) and out-of-phase ( $\chi_m''$ ) signals were observed as a single sharp peak independent of the ac frequency, and the  $T_c$  is determined to be 15.4 K. The  $T_c$  is the highest among PB analogues incorporating a lanthanide ion.<sup>7</sup> The magnetic hysteresis loop of **4** at 2 K shows the coercive field of 140 Oe and the remnant magnetization of  $2.94 \times 10^4 \text{ emu Oe mol}^{-1}$  (Figure 3b). In the case of **3** with diamagnetic La(III) ion, a cusp in the FCM curve, an inflection point around 0.1 kOe of the magnetization curves and ac magnetic behaviors demonstrate a metamagnet-like behavior with  $T_c$  of 7.4 K (Figures 3a,b and S4). These results suggest that the difference of the magnetic behavior between **3** and **4** is caused by the magnetic interaction in the CoLnCo pillar unit. In both cases, a ferromagnetic interaction operates between Co(II) and Cr(III) ions through cyanide bridges within the two-dimensional layers. Here, the constituent CoGdCo complex **2** shows a weak ferromagnetic interaction ( $\theta = +0.76 \text{ K}$  including the orbital contribution of the  $^4T_1$  term of Co(II) ions) between adjacent Co(II) and Gd(III) ions, whereas the CoLaCo complex **1** shows an overall antiferromagnetic behavior with a negative Weiss constant ( $\theta = -12.3 \text{ K}$ ; Figure S3). The magnetic natures of the pillar units are essentially maintained in **3** and **4**, although the magnitude of the magnetic interaction is affected by the aggregation accompanied by structural changes. The antiferromagnetic CoLaCo pillar **1** and the ferromagnetic CoGdCo pillar **2**, respectively, give the metamagnetic phase of **3** and ferromagnetic phase of **4** with a weak antiferromagnetic intersheet dipolar interaction. Each magnetization value at 50 kOe ( $7.36 N\beta$  for **3** and  $14.42 N\beta$  for **4**) is close to a numerical summation of  $[\text{Cr}(\text{CN})_6]^{3-}$  ( $3.00 N\beta$ ) and the respective pillar unit ( $4.37 N\beta$  for **1** and  $11.08$

$N\beta$  for **2**), which also supports the formation of the above-mentioned magnetic phases. Comparing **3** and **4**, the  $T_c$  of **4** is moved upward by the insertion of the Gd(III) ion having a large spin number.

In conclusion, two novel trimetallic assemblies  $[\text{Co}_2\text{Ln}(\text{L})_2(\text{H}_2\text{O})_4][\text{Cr}(\text{CN})_6] \cdot n\text{H}_2\text{O}$  (Ln = La (**3**) and Gd (**4**)) having 3-D pillared-layer structure were prepared by integrating  $[\text{Co}_2\text{Ln}(\text{L})_2(\text{NO}_3)_3] \cdot 4\text{H}_2\text{O}$  (Ln = La (**1**) and Gd (**2**)) and  $K_3[\text{Cr}(\text{CN})_6]$ . The  $\{\text{Co}_2\text{Ln}(\text{L})_2\}$  trinuclear complexes were good precursors to the construction of trimetallic assemblies. Compounds **3** and **4** show a metamagnetic ( $T_c = 7.4 \text{ K}$ ) and a ferromagnetic ( $T_c = 15.4 \text{ K}$ ) behavior, respectively. These are the first examples of 3-D 3d–3d–4f trimetallic magnets, to our best knowledge. The magnetic interaction in the CoLnCo pillar unit plays a key role in the determination of the overall magnetic phase, and the whole magnetic properties can be successfully controlled by the incorporated Ln(III) ions. This research demonstrates a new design strategy of functional materials containing 4f ion(s). Studies on analogous trimetallic compounds,  $[\text{M}_2\text{Ln}(\text{L})_2(\text{H}_2\text{O})_4][\text{M}'(\text{CN})_6]$  (M(II) and M'(III) = 3d metal ions, Ln(III) = 4f metal ions), of different combinations of metal ions are in progress.

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**Supporting Information Available:** Crystallographic data (CIF) and magnetic data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Elemental analysis. (3) Calcd (%) for  $\text{C}_{32}\text{H}_{30}\text{Co}_2\text{CrLaO}_{15}$ : C, 35.54; H, 3.36; N, 10.36. Found: C, 35.31; H, 3.33; N, 10.36. (4) Calcd (%) for  $\text{C}_{32}\text{H}_{34}\text{N}_8\text{Co}_2\text{CrGdO}_{14}$ : C, 35.53; H, 3.17; N, 10.36. Found: C, 35.65; H, 3.00; N, 10.64.
- (11) Crystal data. **3** ( $\text{C}_{32}\text{H}_{30}\text{Co}_2\text{CrN}_8\text{LaO}_{12}$ ):  $M_w = 1027.40$ ,  $T = 183 \text{ K}$ , triclinic, space group  $P1$  (No. 1),  $a = 10.617(4)$ ,  $b = 10.616(4)$ ,  $c = 17.008(6) \text{ \AA}$ ,  $\alpha = 90.014(7)^\circ$ ,  $\beta = 89.982(7)^\circ$ ,  $\gamma = 90.011(6)^\circ$ ,  $V = 1919.0179 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.780 \text{ g cm}^{-3}$ ,  $\mu = 22.93 \text{ cm}^{-1}$ ,  $R1 = 0.053$ ,  $wR2 = 0.151$  (all data),  $\text{GOF} = 1.00$ . **4** ( $\text{C}_{32}\text{H}_{30}\text{Co}_2\text{CrN}_8\text{GdO}_{12}$ ):  $M_w = 1045.74$ ,  $T = 183 \text{ K}$ , triclinic, space group  $P1$  (No. 1),  $a = 10.634(1)$ ,  $b = 10.6385(8)$ ,  $c = 16.878(2) \text{ \AA}$ ,  $\alpha = 89.956(7)^\circ$ ,  $\beta = 89.992(8)^\circ$ ,  $\gamma = 89.904(7)^\circ$ ,  $V = 1919.3298 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.819 \text{ g cm}^{-3}$ ,  $\mu = 29.15 \text{ cm}^{-1}$ ,  $R1 = 0.060$ ,  $wR2 = 0.176$  (all data),  $\text{GOF} = 1.00$ . In both cases, positions of lattice water molecules could not be determined clearly owing to disorder. The initial crystal system was determined as tetragonal; however, it finally fell down to triclinic ( $P1$ ). It can be explained that the high-symmetrical space group was derived from an arrangement of only heavy atoms; however, the ligands in the twisted trinuclear pillar units were not strictly fit for such a high-symmetrical arrangement.
- (12) Figure 1 was drawn using a computer program VENUS: Izumi, F.; Dilanian, R. A. *Recent Res. Dev. Phys.* **2002**, *3* (2), 699. (Transworld Research Network, Trivandrum)

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