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Ferromagnetic Gd–Cu, Tb–Cu, and Ho–Cu Couplings in Isomorphous [Ln_2Cu] Complexes

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Exchange couplings in [{Ln(hfac)$_3$}$_2$Cu(dpk)$_2$] (Hdpk stands for di-2-pyridyl ketoxime) were evaluated by high-frequency electron paramagnetic resonance and magnetization studies, showing ferromagnetic Ln–Cu couplings with $J_{\text{Ln–Cu}}/k_B = +1.271(7)$, $+0.405(3)$, and $+0.196(13)$ K for Ln: Gd, Tb, and Ho, respectively.

Molecule-based magnetic materials have an advantage in designing a spatial arrangement of a variety of magnetic orbitals and preparing low-dimensional frameworks by means of facile self-assembly techniques.[1,2] Heterometallic 4f–3d compounds have been intensively studied for development of single-molecule magnets,[3–5] where strong magnetic anisotropy and large spin are available from lanthanide (Ln) ions.[6] The exchange coupling between 4f and 3d spins is one of the most important parameters, but there have scarcely been direct methods to evaluate them. We are now establishing a standard method to determine quantitatively the exchange couplings[4,7–9] by means of high-frequency electron paramagnetic resonance (HF-EPR) and pulsed-field magnetization.[10] The outline is as follows: (1) Ln ions are treated as Ising spins. (2) Energy levels of spin states are defined by exchange coupling parameters ($J_{\text{Ln–M}}$) at zero field. (3) A Zeeman diagram is drawn, where level crossings take place. (4) Magnetization steps and EPR transitions are assigned.

We newly synthesized [{Ln$^{\text{III}}$(hfac)$_3$}$_2$Cu$^{\text{II}}$(dpk)$_2$] (Ln: Gd, Tb, and Ho; abbreviated as [Ln_2Cu]), where Hhfac stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione and Hdpk for di-2-pyridyl ketoxime. They were characterized by means of X-ray crystallographic analysis[11] together with spectroscopic and elemental analyses.[12] Their molecular structures (Figures 1 and 1S[12]) are isomorphous to that of the known [Dy_2Cu]. The 4f and 3d metal ions are bridged with an O–N group. An inversion center is located at the Cu ion. Each Ln ion forms an eight-coordinated square antiprism.

HF-EPR spectra of powder [Tb_2Cu] were collected in a wide frequency range between 95 and 371 GHz at 4.2 K (Figure 2a). We found a series of major absorptions shifted to a higher field with increasing frequency. As for yellow lines, the g values were 2.022(9) and 2.00(2) from the slope of the frequency-field plot, being consistent with the Cu spin-flip signal satisfying a conventional EPR selection rule of $\Delta m_s = \pm 1$. The line has a negative-field bias from the normal Zeeman effect. Since there is no single-ion anisotropy in Cu spins, the observed characteristic frequency-field relation shows the presence of an internal exchange-bias field at the Cu site. Extrapolation gives a level-crossing field (B_C) of $-3.58(5)$ T for the major $g = 2.022(9)$ line. We obtained $J_{\text{Tb–Cu}} = +0.405(3)$ K from $|J^z| = 6$ for the Tb^{3+} ion ($S = 3$, $L = 3$, $J = L + S = 6$, $g_J = 3/2$), based on the following Ising-type spin-Hamiltonian (eq 1). The z direction is defined with the Ln magnetic easy axis regulated by a crystal field.

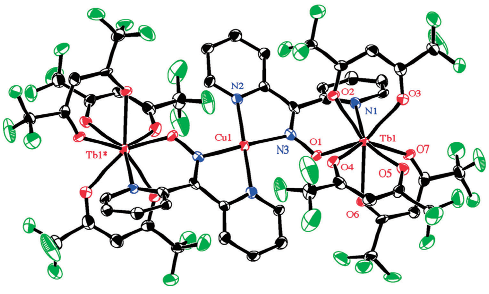

Figure 1. X-ray crystal structure of [Tb_2Cu]. Symmetry operation code of * is $-x$, $2 - y$, $-z$. Hydrogen atoms are omitted for clarity.

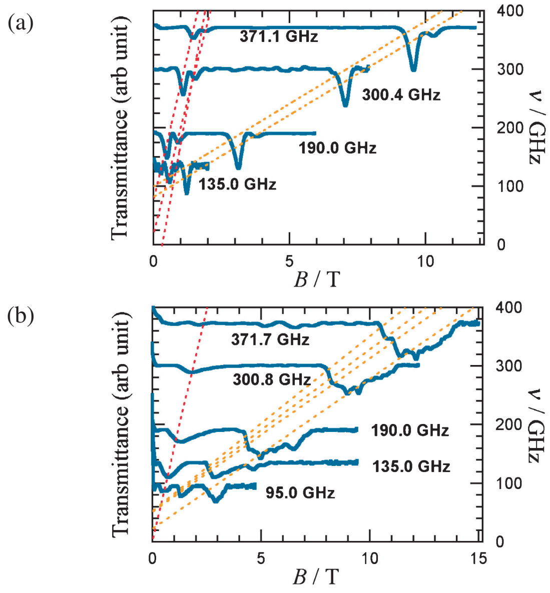

Figure 2. Selected HF-EPR spectra of [Ln_2Cu] measured at 4.2 K [(a) Ln:Tb, (b) Ln:Ho]. The spectra are offset in a linear scale of the frequency. Dotted lines are drawn from linear fitting in the frequency-field plot.

$$\begin{aligned}\hat{H} = &-J_{\text{Ln–Cu}}(\hat{J}^z_{\text{Ln1}} \cdot \hat{S}_{\text{Cu}} + \hat{J}^z_{\text{Ln2}} \cdot \hat{S}_{\text{Cu}}) \\ &+ \mu_B H^z(g_{\text{Ln}} J^z_{\text{Ln1}} + g_{\text{Ln}} J^z_{\text{Ln2}} + g_{\text{Cu}} S_{\text{Cu}}) \end{aligned} \quad (1)$$

Negative and positive B_C's imply the presence of ferro- and antiferromagnetic couplings, respectively. The B_C can be converted to the zero-field energy gap between the ferro- and ferrimagnetic states, which is subsequently related to $J_{\text{Ln–Cu}}$ by the first term in eq 1. When the system has antiferromagnetic coupling, level crossing can be detected as a magnetization step. In the ferromagnetic case like the present study, the magnetization curve will show a featureless increase. Note that variable-frequency EPR is a practical and unique measure to determine precisely a negative B_C.

The g values of the signals with steep slopes denoted by red lines (Figure 2a) were $g =$ ca. 13, 14, and 18, and seem to be caused by transitions among $2J + 1$ multiplets of the Tb ion. A transition of $\Delta m_J = \pm 12$ with $g_J = 3/2$ gives an apparent g value of 18; namely, the observed $g = 18$ transition is ascribable to a forbidden transition with the maximal Δm_J, and the $g = 13$ and 14 transitions are related with smaller Δm_J. The minor Cu signals with $g = 2.00(2)$ may be attributed to a molecule having a Tb ion with thermally populated $|J^z| = 5$. The minor Cu band gave $B_\mathrm{C} = -2.99(8)$ T, which is smaller than that of the major band. It seems to be quite reasonable because B_C is in proportion to $|J^z|$ and the ground $|J^z|$ is 6. If the presence of two Cu signals were attributed to a pair of $g_\parallel$ and $g_\perp$, the two bands should have a common B_C.

HF-EPR spectra of powder [$\mathrm{Ho_2Cu}$] (Figure 2b) also showed several series of signals. The g values of the major bands (yellow lines) were 2.129(17), 1.97(2), 1.87(2), and 1.822(19), which are assigned to the Cu signals. g values smaller than 2 have been reported and discussed for [$\mathrm{Dy_2Cu_2}$]$_n$.[8] Extrapolations of their peaks give different B_C's of $-1.85(7)$, $-1.98(11)$, $-2.05(13)$, and $-0.98(12)$ T, respectively. They may originate in different transitions. The broad peak (a red line) is attributed to the transition in the ground state among $2J + 1$ multiplets of the Ho ion ($S = 2$, $L = 6$, $J = 8$, $g_J = 5/4$). It seems to be a superposition from a few states with different Ho J^z values. Estimation of the exchange parameter $J_\mathrm{Ho\text{–}Cu}$ depends on the J^z value. The Cu bands were somewhat complicated in comparison with those of [$\mathrm{Tb_2Cu}$] and [$\mathrm{Dy_2Cu}$], suggesting distribution of $|J^z|$ values from the $\mathrm{Ho^{3+}}$ ion. However, we can apply eq 1 to each molecule with different J^z.

The ground J^z value can be independently estimated from saturation magnetization (M_S) by SQUID measurements. We have to pay attention to the facts that the molecular arrangement in a monoclinic cell leads to a partial saturation and that field alignment of a polycrystalline specimen is incomplete. The M_S of [$\mathrm{Tb_2Cu}$] was found to be 16 μ_B (1.8 K, 7 T), implying that $|J^z|$ is at least 5. Coexistence of $|J^z| = 5$ and 6 is most likely, in perfect agreement with the EPR results. The M_S of [$\mathrm{Ho_2Cu}$] was 14 μ_B, suggesting $|J^z| = 6$ at least. It has been reported that $\mathrm{Ho^{3+}}$ bisphthalocyaninate anion favors low-lying $|J^z| = 5$, 4, and 6 states.[13] As for [$\mathrm{Ho_2Cu}$], assumption of $|J^z| = 6$ gives $J_\mathrm{Ho\text{–}Cu}/k_\mathrm{B} = +0.196(13)$ K from the strongest band with $g = 1.87(2)$.[14] Furthermore, we confirmed the complete absence of any magnetization step even up to 20 T for [$\mathrm{Tb_2Cu}$] and [$\mathrm{Ho_2Cu}$] in pulsed-field measurements,[10b] supporting that they are ground ferromagnetic molecules.

The HF-EPR spectra of spin-only [$\mathrm{Gd_2Cu}$] ($S = 7/2$ for $\mathrm{Gd^{3+}}$) were measured, but the $g = 2$ line showed no bias field[15] (Figure 2S[12]). As an alternative method, we measured $\chi(T)$ and $M(B)$ on a SQUID (Figure 3S[12]). The $\chi_\mathrm{m}T$ value monotonically increased on cooling, indicating that [$\mathrm{Gd_2Cu}$] is a ground ferromagnetic molecule. The $J_\mathrm{Gd\text{–}Cu}$ was determined according to the van Vleck equation involving Heisenberg spins, giving $J_\mathrm{Gd\text{–}Cu}/k_\mathrm{B} = +1.271(7)$ K with $g_\mathrm{avg} = 1.9826(9)$. The magnetization curve is consistent with $S_\mathrm{total} = 15/2$.

The present result is in sharp contrast to previous experiments with [$\mathrm{Dy_2Cu}$].[9] The Cu signals exhibited a V-shape with a positive B_C of $+1.36$ T in the frequency-field plot for [$\mathrm{Dy_2Cu}$], from which we derived $J_\mathrm{Dy\text{–}Cu}/k_\mathrm{B} = -0.126(3)$ K.[9]

We conclude that the Gd–, Tb–, and Ho–Cu couplings are ferromagnetic with $J_\mathrm{Ln\text{–}Cu}/k_\mathrm{B} = +1.271(7)$, $+0.405(3)$, and $+0.196(13)$ K, respectively, whereas the Dy–Cu coupling is antiferromagnetic, although they are all isomorphous.[16] There have been many reports on ferromagnetic $J_\mathrm{Gd\text{–}Cu}$.[17,18] Kahn et al. explained the ferromagnetic couplings between $\mathrm{Cu^{2+}}$ and heavy Ln ions.[18] The orbital and spin momenta of Ln are parallel, and the ferromagnetic spin–spin coupling gives rise to an overall ferromagnetic interaction. It is reasonable that the Tb and Ho derivatives have ferromagnetic coupling like the Gd derivative.

Thanks to the high resolution of HF-EPR and variable-frequency techniques, the 4f–3d magnetic couplings are definitively determined. This technique will contribute the development of science and technology of 4f-based magnets.

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12 For the synthetic details, the X-ray crystal structures of [$\mathrm{Gd_2Cu}$] and [$\mathrm{Ho_2Cu}$], and the HF-EPR and magnetic studies on [$\mathrm{Gd_2Cu}$], see Supporting Information, being available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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14 Possibility of $|J^z| = 7$ or 8 for the Ho ion is not completely rejected; we obtained $J_\mathrm{Ho\text{–}Cu}/k_\mathrm{B} = +0.172(11)$ K from $|J^z| = 8$. A cautious conclusion would be $J_\mathrm{Ho\text{–}Cu}/k_\mathrm{B} = +0.18(2)$ K.

15 The $g = 2$ signal can be assigned to the transition in the $S_\mathrm{total} = 15/2$ multiplet. The EPR selection rule tells us that the transition to any states of the $S_\mathrm{total} = 13/2$ multiplet is forbidden. On the other hand, it is violated for the other [$\mathrm{Ln_2Cu}$] compounds, because of the admixture of the orbital angular momentum and lowered symmetry.

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