



Exchange couplings in one-dimensionally arrayed 4f–3d heterometallic $[\text{Ln}_2\text{Cu}_2]_n$ compounds: A chemical trend of the coupling parameter

Atsushi Okazawa^a, Kei Fujiwara^b, Ryo Watanabe^b, Norimichi Kojima^a, Shunsuke Yoshii^c, Hiroyuki Nojiri^c, Takayuki Ishida^{b,*}

^a Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo 153-8902, Japan

^b Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

^c Institute for Materials Research and CINTS, Tohoku University, Katahira, Sendai 980-8577, Japan

ARTICLE INFO

Article history:

Available online 10 March 2011

Keywords:

EPR
ESR
Single-molecule magnet
Lanthanoid
Lanthanide
Rare earth metal
Exchange interaction

ABSTRACT

Heterometallic polymeric coordination compounds $[\{\text{Ln}(\text{hfac})_2(\text{CH}_3\text{OH})\}_2\{\text{Cu}(\text{dmg})(\text{Hdmg})\}_2]_n$ (abbreviated as $[\text{Ln}_2\text{Cu}_2]_n$) involving light lanthanoid ions, Pr, Nd, Sm, and Eu, were synthesized, where H₂dmg and Hhfac stand for dimethylglyoxime and 1,1,1,5,5,5-hexafluoropentane-2,4-dione, respectively. The X-ray crystallographic analysis shows that their structures are isomorphous to those of the known heavy lanthanoid analogs. The exchange couplings were evaluated by high-frequency electron paramagnetic resonance and pulsed-field magnetization studies, giving ferromagnetic exchange parameters: $J_{\text{Pr-Cu}}/k_B = 0.039(1)$ K, $J_{\text{Nd-Cu}}/k_B = 0.38(1)$ K, $J_{\text{Sm-Cu}}/k_B = 0.95(2)$ K, and no interaction between Eu and Cu ions. A significant trend is found in the order of the periodic table. The ferro- and antiferromagnetic 4f–3d couplings were characterized for the light and heavy lanthanoid derivatives, respectively. The magnitude of $J_{\text{Ln-Cu}}$ decreases with a decrease of the 4f-spin portion, i.e., the number of unpaired electrons, whether the coupling is ferro- or antiferromagnetic.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Single-molecule magnets (SMMs) exhibit magnetic hysteresis from the single-molecular origin [1]; namely, slow magnetization reversal due to a high energy-barrier. Lanthanoid ions seem suitable for development of SMMs, since the barrier is caused by strong magnetic anisotropy and large spins [2,3]. Several Dy–Cu compounds showed slow magnetization reversal and distinct hysteresis, as clarified by ac susceptibility and pulsed-field magnetization measurements [4–10]. We have investigated the exchange couplings and energy-level structures of them [4–7] by means of combined methods of high-frequency electron paramagnetic resonance (HF-EPR) [11] and pulsed-field magnetization [12]. One of the advantages of HF-EPR is the ability of precise determination of the 4f–3d exchange coupling parameter (J_{4f-3d}) owing to the high resolution and variable-frequency technique [13]. We have established a standard method to evaluate J_{4f-3d} [4–7], and a distinct chemical trend in J_{4f-3d} has been successfully characterized in the simplest dinuclear systems [14].

We have reported the HF-EPR study on heterometallic chain compounds $[\{\text{Ln}(\text{hfac})_2(\text{MeOH})\}_2\{\text{Cu}(\text{dmg})(\text{Hdmg})\}_2]_n$ having heavy lanthanoid ions (abbreviated as $[\text{Ln}_2\text{Cu}_2]_n$ hereafter; Ln = Tb,

Dy, Ho, and Er; Hhfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione; H₂dmg = dimethylglyoxime) [6,7]. The energy-level crossing and quantum tunneling of magnetization were explained in terms of the well-defined Ln–Cu exchange couplings. Although they form a one-dimensional chain structure, their magnetic properties can be described in terms of SMMs rather than single-chain magnets. The J_{4f-3d} values were determined, and, the most interestingly, the magnitude of J_{4f-3d} monotonically decreased in the order of Gd, Tb, Dy, Ho, and Er [6,7,15]. We will report here the characterization of various isomorphous $[\text{Ln}_2\text{Cu}_2]_n$ complexes having light lanthanoid ions and their magnetic properties, where Ln is Pr, Nd, Sm, and Eu. Comparison of the 4f–3d exchange interactions over the entire 4f-metal ion series is of great interest. A clear relation between J_{4f-3d} and the 4f atomic number (Z) will be presented.

2. Results

2.1. Crystallographic study

Complexes $[\text{Pr}_2\text{Cu}_2]_n$, $[\text{Nd}_2\text{Cu}_2]_n$, $[\text{Sm}_2\text{Cu}_2]_n$, and $[\text{Eu}_2\text{Cu}_2]_n$ (for the molecular structures, see Fig. 1) were prepared according to the literature method [6,7,15] using the corresponding Ln salt as a starting material. They crystallized in a triclinic $P\bar{1}$ space group. Their molecular structures are isomorphous to each other and also to those of $[\text{Gd}_2\text{Cu}_2]_n$ [15] and heavy $[\text{Ln}_2\text{Cu}_2]_n$ [6,7]. Selected

* Corresponding author. Tel.: +81 42 443 5490; fax: +81 42 443 5501.

E-mail address: ishi@pc.ucc.ac.jp (T. Ishida).

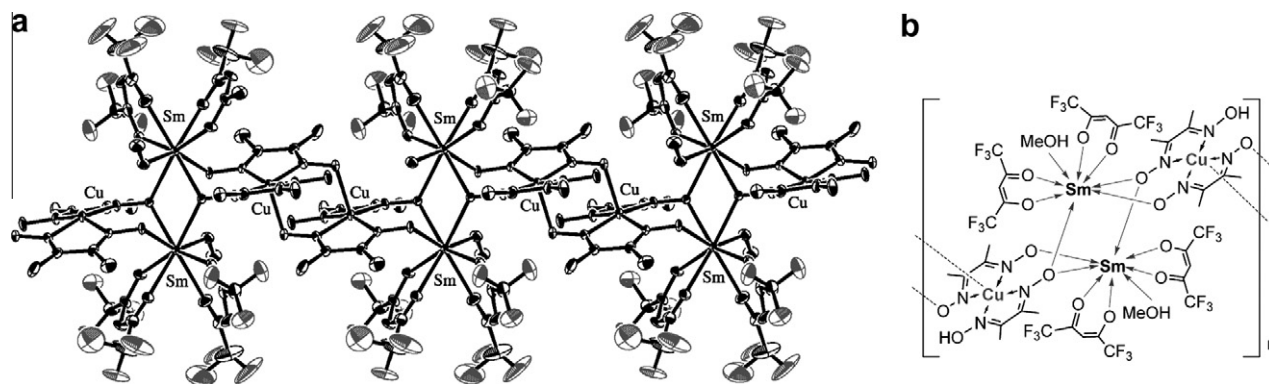


Fig. 1. (a) Crystal structure of $[\text{Sm}_2\text{Cu}_2]_n$ with the thermal ellipsoids at the 50% probability level. Three repeating units are shown. Hydrogen atoms are omitted for clarity. (b) Structural formula of $[\text{Sm}_2\text{Cu}_2]_n$. Note that the Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er derivatives are all isomorphous.

crystallographic parameters of the present derivatives are listed in Table 1. The lanthanoid contraction in ionic radius is clearly demonstrated; for example, the unit cell volume is monotonically shrunk from Ln = $_{59}\text{Pr}$ ($V = 1552.0(17) \text{ \AA}^3$) to $_{68}\text{Er}$ ($V = 1509(2) \text{ \AA}^3$) [7].

Fig. 1 shows the X-ray crystal structure of $[\text{Sm}_2\text{Cu}_2]_n$ for an instance. The monomeric unit was a diamond-arranged Sm_2Cu_2 and the symmetrical inversion center is located in the center of a diamond; a half of a diamond is crystallographically independent. There are two Sm–Cu relations. The Sm ion has a square-antiprism structure with eight oxygen atoms coordinated. The magnetic orbital of the Cu^{2+} ion is $3d_{x^2-y^2}$, which is located in the $[\text{Cu}(\text{dmg})(\text{Hdmg})]^-$ basal plane, and accordingly the Ln–Cu exchange interaction across the diatomic O–N bridge will be appreciable. On the other hand, the interaction between the $[\text{Ln}_2\text{Cu}_2]$ units is very weak because of the out-of-plane bridging structure with the axial $\text{O} \cdots \text{Cu}$ coordination [6,7,15]. No appreciable inter-chain interaction was found, and accordingly the chains are magnetically isolated.

2.2. Magnetic study

The pulse-field magnetization data on a polycrystalline specimen of $[\text{Pr}_2\text{Cu}_2]_n$ were collected at 0.5 K (Fig. 2a). The magnetization at 19 T was $4.4\mu_B$ and did not show saturation, which can be

compared with the calculated saturation value (M_s) $6.80\mu_B$ with $|J^z| = 3$ and $g_J = 4/5$ for a Pr^{3+} ion. A parallel study on the same specimen using a SQUID magnetometer at 2 K supported this result. The field-oriented data were usually obtained in these measurements (see Section 5), but the M_s may not be a full-saturation value because of incomplete orientation. The slope around 19 T is partly explained by such incomplete orientation as well as a possible shift of the population distribution to the ground magnetic states with large $|J^z|$. This finding indicates that the M_s is given by $|J^z| = 3$ and that the contribution of the thermally populated to smaller $|J^z|$ states located close to that of $|J^z| = 3$.

In sharp contrast to the results on the heavier $[\text{Ln}_2\text{Cu}_2]_n$ (Ln = Tb, Dy, Ho, and Er), the magnetization curve of $[\text{Pr}_2\text{Cu}_2]_n$ did not show any step up to 20 T. When the specimen has a relatively weak Ln–Cu antiferromagnetic coupling, a copper spin flip is observed as a magnetization jump. There are two possible explanations for the absence of any step. One is that the specimen involves Ln–Cu ferromagnetic coupling. Another possibility is the presence of antiferromagnetic coupling with a larger coupling constant than the upper limit of the experimental window, but it is less likely, because 4f–3d interactions are usually small and detectable below 20 T.

Similarly, the pulsed-field magnetization on a polycrystalline specimen of $[\text{Nd}_2\text{Cu}_2]_n$ was measured at 0.5 K (Fig. 2a). The magnetization at 19 T was $6.2\mu_B$ and did not show saturation, in

Table 1
Selected crystallographic data for $[\text{Ln}_2\text{Cu}_2]_n$ (Ln = Pr, Nd, Sm, and Eu).

Compounds	$[\text{Pr}_2\text{Cu}_2]_n$	$[\text{Nd}_2\text{Cu}_2]_n$	$[\text{Sm}_2\text{Cu}_2]_n$	$[\text{Eu}_2\text{Cu}_2]_n$
Formula	$\text{C}_{19}\text{H}_{19}\text{CuF}_{12}\text{N}_4\text{O}_9\text{Pr}$	$\text{C}_{19}\text{H}_{19}\text{CuF}_{12}\text{N}_4\text{NdO}_9$	$\text{C}_{19}\text{H}_{19}\text{CuF}_{12}\text{N}_4\text{O}_9\text{Sm}$	$\text{C}_{19}\text{H}_{19}\text{CuEuF}_{12}\text{N}_4\text{O}_9$
Formula weight	879.81	883.15	889.31	890.87
Habit	brown prism	brown prism	brown prism	brown prism
Dimension (mm^3)	$0.26 \times 0.12 \times 0.07$	$0.55 \times 0.40 \times 0.08$	$0.21 \times 0.21 \times 0.11$	$0.25 \times 0.25 \times 0.10$
T (K)	90	90	90	100
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (\AA)	10.594(5)	10.582(5)	10.5915(8)	10.5801(5)
b (\AA)	11.171(7)	11.177(8)	11.1239(5)	11.1315(6)
c (\AA)	14.237(11)	14.238(10)	14.1921(5)	14.1870(9)
α ($^\circ$)	71.84(6)	71.70(5)	71.710(6)	71.642(4)
β ($^\circ$)	75.79(6)	76.10(6)	75.908(6)	75.948(3)
γ ($^\circ$)	85.28(7)	85.16(6)	85.090(7)	84.955(3)
V (\AA^3)	1552.0(17)	1551.9(17)	1539.77(16)	1538.22(16)
Z	2	2	2	2
D_{calc} (g cm^{-3})	1.883	1.890	1.918	1.923
Unique data	6966	7041	6925	6821
μ ($\text{Mo K}\alpha$) (mm^{-1})	2.353	2.460	2.706	2.830
R (F) ^a ($I > 2\sigma(I)$)	0.0334	0.0535	0.0518	0.0595
R_w (F^2) ^b (all data)	0.0471	0.1062	0.1046	0.1353

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Download English Version:

<https://daneshyari.com/en/article/1335991>

Download Persian Version:

<https://daneshyari.com/article/1335991>

[Daneshyari.com](https://daneshyari.com)