The Hardest Magnet from a Coordination Polymer of Alternating Cobalt(II)–Radical Heterospins

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A coordination polymer [Co(hfac)$_2$•L] (L = *o*-ethoxyphenyl nitronyl nitroxide) was prepared, structurally characterized, and revealed to show a record coercive field of 54 kOe at 6 K. The magnetic easy axis was found to be perpendicular to the chain direction. Interchain dipolar coupling is important for the bulk and/or single-chain properties in this series.

There have been a plethora of examples of low dimensional complexes containing nitronyl nitroxide (NN) radicals[1] with metal 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hfac) salts, developed in pursuit of metal–radical hybrid magnets.[2] Since the discovery of the first single-chain magnet (SCM) [Co(hfac)$_2$•*p*-methoxyphenyl-NN] (**1**) by Gatteschi et al.,[3] several derivatives have been extensively investigated toward use as novel SCMs.[4] We have found interplay between SCM and bulk character in [Co(hfac)$_2$•*p*-butoxyphenyl-NN] (**2**).[5] This compound showed a giant coercivity of 52 kOe at 6 K. The long-range order has been confirmed by a muon spin rotation/relaxation study.[6]

To investigate the magneto–structure relationship of this type of compound, we have prepared an ortho derivative [Co(hfac)$_2$•*o*-ethoxyphenyl-NN] (**3**). We tried complexations using meta derivatives, but the resultant compounds were not suitable for further structural or magnetic characterization.

Compound **3** was synthesized according to a conventional method.[2–5] The crystal structure has been determined as a $P2_1/n$ space group (Figure 1), though the refinement was somewhat unsatisfactory because of small crystal size.[7] There are two chains in the crystal lattice, which are symmetrically correlated. Each chain has a 2_1 screw symmetry along the crystallographic *b* axis. The radical oxygen atoms are located in a cis manner around the Co ions. The intrachain Co···Co distance (7.52 Å) is shorter than the interchain distances (10.87 Å and longer).

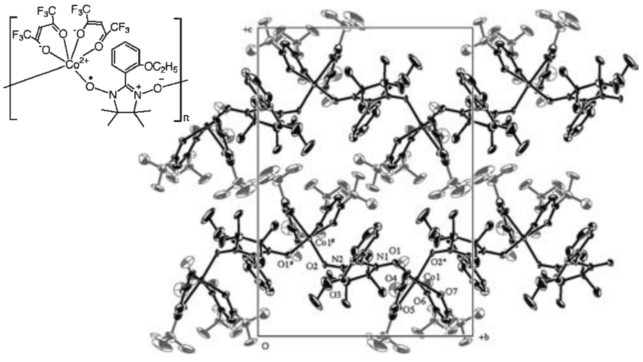

Figure 1. (Left) Structural formula of **3**. (Right) X-ray crystal structure of **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Trifluoromethyl groups are shaded.

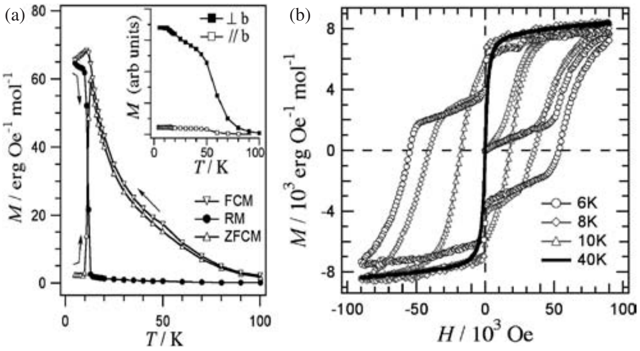

Figure 2. (a) FCM (field-cooled magnetization), RM (remnant magnetization), and ZFCM (zero-field-cooled magnetization) for polycrystalline **3** with the applied field of 5 Oe. Inset: FCM curves for aligned single crystals. The field of 500 Oe was applied in the directions parallel and perpendicular to the *b* axis. (b) Hysteresis loops of polycrystalline **3**. The field scan rate was constant at 18 Oe s^{-1}.

We measured static magnetic properties of **3**. A ferrimagnetic chain was confirmed by the $\chi_{\mathrm{mol}}T$ upsurge on cooling in the $\chi_{\mathrm{mol}}T$ vs. T plot (Figure 1S, Supporting Information).[15] The Curie–Weiss analysis on the data in 100–300 K gave $C = 1.71 \pm 0.03\,\mathrm{cm^3\,K\,mol^{-1}}$ and $\theta = 106 \pm 2\,\mathrm{K}$.

FCM, RM, and ZFCM experiments on **3** were performed (Figure 2a). The FCM very gradually increased on cooling and finally reached a saturation value at 10 K. The RM rapidly disappeared at 10 K. The ZFCM was hardly magnetized and started to increase at 10 K on heating. Usually such behavior below 10 K is described as being magnetically "hard"[8] and may be potentially utilized as permanent magnets with strong hysteresis. A quantitative indicator for hard character is the coercivity, which can be measured as a coercive field (H_{C}), or a hysteresis width, in the *M*–*H* curves.

As Figure 2b shows, the magnetization of **3** almost saturated to a value of $8.5 \times 10^3\,\mathrm{erg\,Oe^{-1}\,mol^{-1}}$ at 9 T,[9] which satisfactorily agrees with a residual moment from the ferrimagnetic Co and NN spins. Below 10 K, **3** behaved as a very hard magnet showing a wide hysteresis loop. A coercive field (H_{C}) was 54 kOe at 6 K, being a record slightly larger than that of **2** (52 kOe at 6 K).[5] Interestingly, the H_{C} was sensitive to temperature, suggesting that the growth of the magnetic hardness is related to the freezing of the dynamics of magnetization reorientation. A magnetization jump was found at zero field, in sharp contrast to the result on **2**. The origin is not clear so far, but it may be related with quantum tunneling.

From 10 to ca. 40 K, **3** was very easily magnetized and demagnetized (Figure 2a). The magnetization curve at 40 K exhibited a sharp rectangular S-shape without any hysteresis (Figure 2b). Such ferromagnetic materials are said to be magnetically "soft."[8] The chain has a ground ferrimagnetic state,[2–5] and accordingly the ferromagnetic character should be attributed to the interchain coupling. The magnetic phase transition temperature of **3** has not been determined yet, but the long-range ordering of **2** has been shown to occur at 40 K.[6]

The ac magnetic susceptibilities of **3** were measured, and frequency dependence was observed (Figure 3a). A half-circle was clearly drawn in the Cole–Cole plot (the inset). The simulated curve with $\alpha = 0.138 \pm 0.009$ well reproduced the experimental data.[10] The small α guarantees the presence of the single relaxation pathway.

The Arrhenius analysis, based on the equation $\ln(2\pi\nu) = -\ln(\tau_0) - E_a/k_BT$, afforded the large activation energy for magnetization reorientaion, $E_a/k_B = 357 \pm 10$ K, with $\tau_0 = (3.3 \pm 1.8) \times 10^{-12}$ s for **3** (Figure 3b). The extrapolation with $\nu = 10^{-4}$ Hz (i.e., τ becomes hours) gave an apparent critical temperature of 10.6 K. This value is perfectly consistent with the results of Figure 2a. The E_a of **3** is much larger than that of **1** as a SCM ($E_a/k_B = 154(2)$ K).[3]

The dynamics was also monitored by the remnant decay as a function of time. Almost permanent magnetization of **3** was recorded at 5 K, and a negligible decay at 10 K. On the other hand, the magnetizations at 12 and 15 K exhibited considerably fast relaxing (Figure 2S, Supporting Information).[15] They were analyzed according to a single stretched exponential function, $M = M_0 \exp[-(kt)^\gamma]$.[11] We confirmed the Arrhenius behavior on these data together with the ac susceptibility ones (Figure 3b). Only a slight downward deviation was observed for the RM data, which may be attributed to quantum tunneling of the magnetization,[10] as supported by the magnetization jump at zero field (Figure 2b). Tunneling is more significant at lower temperatures in comparison with that of the Arrhenius regime.

The apparent critical behavior around 10 K (Figures 2 and 3a) is due to the time scale of experimental tools such as dc and ac magnetometers to see the stabilization of the hard magnet state. The magnetic hardness gradually grows on cooling, which seems to be related to the dynamics of domain wall movement.[5] The long-range ordering of **3** might take place somewhere above 10 K like **2**.

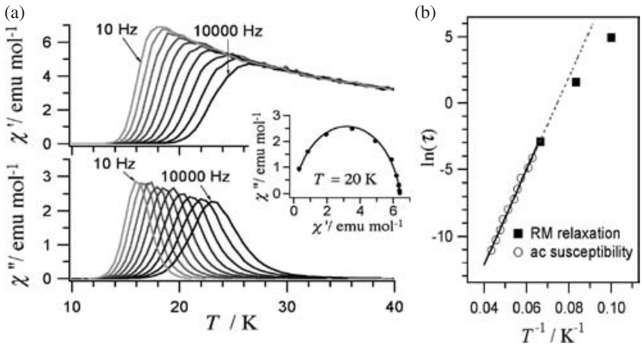

Figure 3. (a) Ac magnetic susceptibilities χ' and χ'' of polycrystalline **3**. The ac field amplitude was 5 Oe. Inset: the Cole–Cole plot at 20 K. The solid line represents the calculation with $\alpha = 0.138$. (b) Arrhenius plot on the time constant ($\tau = 1/k$) against T^{-1} from the data of the ac susceptibility and RM relaxation for **3**. A line stands for the best fit of the ac susceptibility data with $E_a/k_B = 357$ K.

We obtained relatively large single crystals of **3** and studied the magnetic anisotropy on its aligned mosaic crystals (the inset of Figure 2a). The magnetic easy axis was found to be located perpendicular to the chain direction, and the hard axis in the chain direction. This situation is similar to that of **2**.[5] This kind of anisotropy favors dipolar ferromagnetic coupling among the chains. On the other hand, **1** has a 3_1 screw symmetry with the magnetic easy axis in the chain direction.[3] The classical dipolar coupling among the chains depends on the direction of magnetic easy and hard axes, which is important for the bulk properties.[12,13]

It seems essential that the easy axes of **3** and **2** lie perpendicular to the chain direction to afford the interchain dipolar ferromagnetic coupling. The exchange coupling of Co–radical spins is directly related with E_a, as proposed by Glauber.[14] Domain wall motion involves the magnetization reversal of each chain in a wall width. In the present case, a kink moves within a chain but in a collective manner owing to the appreciable interchain interaction, thus giving the large E_a. The sizable interchain coupling also leads to the relatively high T_N. Therefore, the classical dipolar coupling is versatile for the development of high T_N (T_C) and high H_C magnets.[15]

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7 Selected data: $C_{25}H_{23}CoF_{12}N_2O_7$, monoclinic $P2_1/n$, $a = 11.084(3)$, $b = 13.954(4)$, $c = 20.209(6)$ Å, $\beta = 97.566(3)°$, $V = 3098.5(15)$ Å^3, $Z = 4$, $d_{cal} = 1.608$ g cm^{-3}, μ(Mo Kα) = 0.671 mm^{-1}, $R_{int} = 0.120$, $R(F)$ ($I > 2\sigma(I)$) = 0.0847, $R_w(F^2)$ (all data) = 0.2233, $T = 100$ K for 6667 unique reflections. CCDC reference number 728253.

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9 The magnetization did not reach the saturation value even at 9 T below 6 K because of the hard character.

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15 For the $\chi_{mol}T$ vs. T plot in the applied field of 500 Oe and RM relaxation after applying and removing 50 Oe for **3**, see Supporting Information, being available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.