**Giant Coercivity**

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# Record Hard Magnets: Glauber Dynamics Are Key**

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Magnetism, and in particular the force that magnetic materials exert at a distance, have fascinated mankind from the beginning of civilization. A material exposed to a magnetic field can retain its magnetized state after the field is removed. The magnetization in this case is cancelled only by applying a field in the opposite direction. The larger the field required to cancel the magnetization, also known as coercive field $H_c$, the harder the magnet. Very hard magnets are important for mechanical devices, and nowadays they are based on intermetallic compounds, mainly SmCo and NdFeB alloys. However, a comparison of hardness based on the coercive field is made difficult by the strong dependence of $H_c$ on the preparation process, because the irreversible motion of the domain walls is heavily affected by defects, grain boundaries, and so forth.

To date, molecular magnetism has failed to provide materials that at high temperature can compete with metallic hard magnets. Nevertheless, it has played a crucial role in low-dimensional magnetism. In fact, the appropriate choice of building blocks and linkers out of a huge library allows for an efficient confinement of the magnetic interaction. In particular, molecular magnetism has shown that magnetic hysteresis can be observed in the absence of long-range magnetic order in materials in which the magnetic interaction is either restricted to zero dimensions (that is, it has a finite length in three dimensions) or is confined in one dimension.[1]

Polynuclear clusters[2] and chains[3] are now being widely investigated for their ability to retain a magnetic memory of purely molecular origin as well as for interesting quantum effects.[4] These two classes of materials have been given the evocative names single molecule magnets, SMM,[5] and single chain magnets, SCM,[6] respectively.

For SCM, the possibility to observe the freezing of the magnetization was predicted in the 1960s by Glauber,[7] who developed the kinetic model for a chain of ferromagnetically coupled spins showing Ising-type anisotropy, that is, the spin is confined in one direction and can assume only the up/down configurations. In this case, the hysteresis results from the progressive slowing of the relaxation mechanism as its characteristic time, $\tau$, diverges exponentially at low temperature [Eq. (1)]

$$\tau = \tau_0 \exp(\Delta E / k_B T) \qquad (1)$$

The barrier $\Delta E$ is given by the energy required to nucleate two domain walls, that is, inverting the direction of one spin as shown in Figure 1. This energy is proportional to the intrachain exchange interaction $J_{\text{intra}}$. For the Ising Hamiltonian written as $\mathscr{H} = JS^2\Sigma\sigma_i\sigma_{i+1}$ (where $\sigma$ can only assume the values $\pm 1$, and $S$ is the spin value), the energy difference becomes $\Delta E = 4S^2J_{\text{intra}}$.

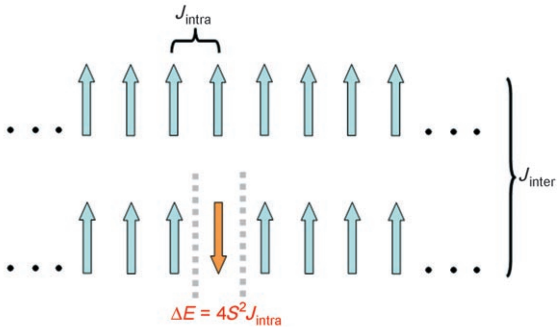

*Figure 1.* In the ferromagnetic chain of Ising spins, the relaxation of the magnetization requires the nucleation of a reversed domain, and it costs four times the nearest-neighbor exchange energy. The 3D magnetic order, however, relies on much weaker interchain interactions.

The first system to be well rationalized with the Glauber model was a cobalt(II) chain[8] in which the metal ions are linked by nitronyl-nitroxide radicals (Figure 2, top). These radicals have the unpaired electron essentially delocalized on the two NO groups and are particularly efficient in transmitting the magnetic interaction. They are versatile because their properties can be tuned by changing the substituents attached to the five-membered ring.

Recently Ishida and co-workers[9] reported an analogous derivative with a slightly modified NIT-$C_6H_4$-O-R radical in which the original methyl group (**1**, $R = CH_3$) is substituted by the longer *n*-butyl group (**2**, $R = (CH_2)_3CH_3$; Figure 2).

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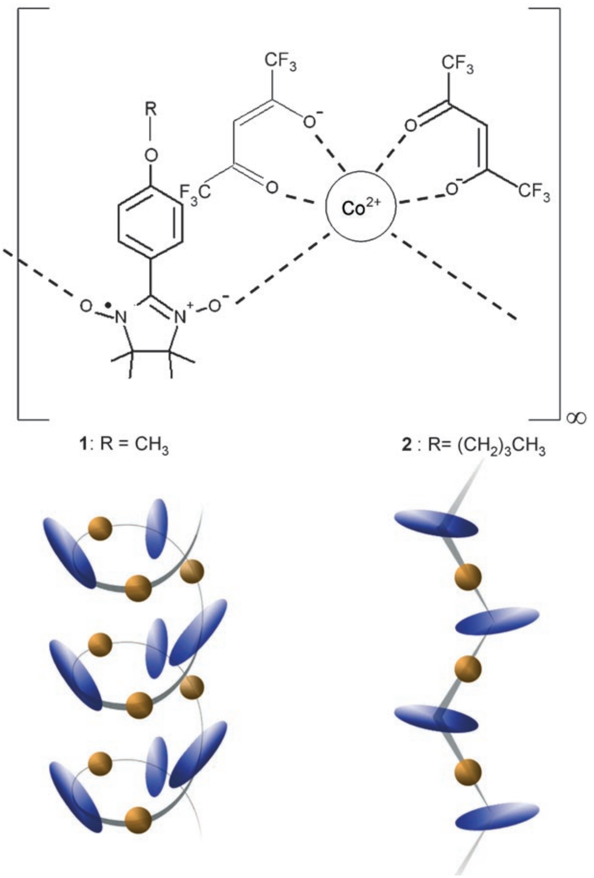

***Figure 2.*** Top: Schematic view of the chemical structure of the chain compounds [Co(hfac)$_2$NIT-C$_6$H$_4$-O-R]$_\infty$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, NIT = nitronyl-nitroxide radical). Bottom: The 1D arrangement of the Co$^{II}$ spin centers (blue ellipsoids) and radical centers (orange spheres). The mutual orientation of the Co$^{II}$ easy axes (the elongation axes of the ellipsoids) is different between **1** (the chain is a trigonal helix) and **2** (a binary screw).

Surprisingly, **2** shows more efficient interchain interactions and, according to the authors, orders magnetically around 45 K. It shows a very large coercive field of 52 kOe at 6 K (Figure 3); for comparison, the record value is 44 kOe at room temperature for commercial SmCo$_5$. Even if only a preliminary characterization of **2** is available, it is interesting to try to correlate these two interesting findings to the molecular nature of the compound.

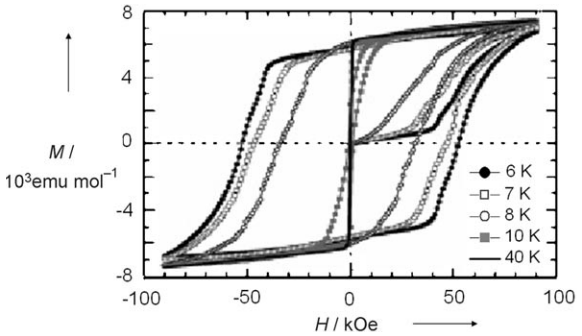

***Figure 3.*** Temperature dependence of the hysteresis loop of a powder sample of **2** recorded at different temperatures between 6 K and 40 K. Extracted with permission from reference [9]. Copyright *J. Am. Chem. Soc.* **2008**.

Ishida and co-workers' study seems to contradict the common intuition that bulkier ligands can better shield one chain from another, thus lowering the temperature at which magnetic order sets in. However, when dealing with anisotropic metal ions such as Co$^{II}$, other factors have to be taken into account. For instance, in **1** the chain structure is generated by a threefold screw axis of the trigonal space group. Thus, the easy axes of adjacent cobalt ions are not collinear but almost perpendicular to each other (Figure 2, bottom). This situation was well evidenced by the reduced magnetic anisotropy of **1** compared to that estimated from studies on the monomeric compound.[10] Non-collinearity of the easy axes of adjacent spins is much more common in molecular magnetism than in traditional systems. In fact, it usually originates from the presence of a crystal symmetry that is higher than the symmetry of the magnetic sites, as these often have very low symmetry owing to the use of different ligands to fulfill different functions.

In **2**, the substitution of a residue far from the NO groups is not expected to modify directly the electronic and magnetic properties of the cobalt ions, but the change is sufficient to induce a significantly different crystal packing. The chain is now generated by the binary screw axis of the monoclinic space group, and the data reported by Ishida and co-workers suggest that the easy axes are now more nearly parallel to each other and almost perpendicular to the chain (Figure 2). This situation favors ferromagnetic dipolar interchain interactions, while in **1** the stronger non-collinearity reduces dipolar interactions.

It is apparent that the molecular nature of the materials makes it possible to go from SCM behavior to 3D magnetic ordering by minor modifications on the periphery of the ligands. More intriguing is the very high coercive field of **2**.[9] It is not straightforward to compare the results obtained by Ishida and co-workers at low temperature with measurements on traditional hard magnets at room temperature. In fact, an increase of $H_c$ at low temperature is also expected for metallic materials; however, it is not as dramatic as the one evidenced by Figure 3.[11] More studies are needed to fully clarify the origin of the large $H_c$ observed in **2**, but it is interesting that below the ordering temperature the relaxation time of the magnetization diverges exponentially as in an SCM. The value of $\Delta E$ (360(6) K) is almost double that observed in **1** but is still compatible with the strong intrachain interaction between metal ions and nitronyl-nitroxide radicals[10] and could also contribute to the magnetic ordering observed in **2**.

The Glauber dynamics in **1** and **2** therefore seem very robust. They are hardly affected by interchain interactions and even by the phase transition, as predicted theoretically.[12] Could the underlying Glauber dynamics be at the origin of the exceptional hardness of the material? As shown in Figure 1, the magnetic ordering in a quasi 1D material results from the interplay of the strong intrachain interactions, which are responsible for the spin correlation in the chain, and the much weaker interchain interactions. The latter limit the transition temperature of chain-based magnetic materials. However, the reversal of the magnetization in such anisotropic materials seems to occur through the nucleation of walls in the chains, in which case only the very strong intrachain interactions enter into play, giving rise to a giant coercivity despite the relatively low ordering temperature.

At the level of characterization of Ishida and co-workers' recent communication, any rationalization remains speculative. Nevertheless, it is undoubted that SCM have revealed another fascinating aspect: when 1D units undergo a phase transition to 3D magnetic order, a very large coercivity appears and increases so pronouncedly at low temperature as to make these materials comparable to the hardest rare-earths-based alloys. Interestingly, the previous record of $H_c$ among molecular magnets was held by another system based on 1D $Mn^{III}$ units bridged by organic radicals.[13] $Mn^{III}$ is another paramagnetic ion with easy axis anisotropy, on which most known SCM are based.[3,14]

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