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Bimetallic Molecular-Based Magnets with Large Coercive Fields

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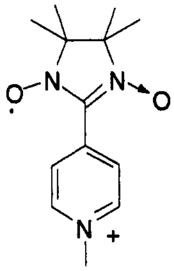
The first molecular-based magnets were reported in 1986.[2-4] The strategy developed in our group consists of assembling high-spin molecules, ferrimagnetic chains, or planes within the crystal lattice in a ferromagnetic fashion.

Recently we described a series of compounds of formula $(cat)_2Mn_2[Cu(opba)]_3{\cdot}S$, where cat^+ is a monovalent cation, opba is *ortho*-phenylenebis(oxamato), and S stands for solvent molecules.[5] These compounds exhibit a spontaneous magnetization below critical temperatures ranging from 12 to 22.5 K. The structure of one of these compounds has been solved. It is essentially two-dimensional. Each layer consists of edge-sharing hexagons with a Mn(II) ion in a chiral distorted octahedral environment at each corner, and a Cu(II) ion in an elongated tetragonal environment at the middle of each edge, as recalled in Figure 1. When cat^+ is the nitronyl nitroxide radical cation 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide, hereafter abbreviated as rad^+:



two nearly perpendicular networks of layers stacking on each other interpenetrate, affording a fully interlocked three-dimensional structure. rad^+ cations connect the Cu(II) ions of a network to those of the nearly perpendicular network.[6]

All these $(cat)_2Mn_2[Cu(opba)]_3{\cdot}S$ compounds are soft magnets. The magnetization versus magnetic field curves below T_c show hysteresis loops with weak coercive fields, of the order of 10 Oe at 4.2 K. The value of the coercive field at a given temperature for a polycrystalline magnet depends on both the chemical nature of the compound and some structural factors like the size and the shape of the grains within the sample.[7] Concerning the chemical nature of the compound, the key role is played by the magnetic anisotropy of the spin carriers which prevents the domains to rotate freely when applying the field.[7,8]

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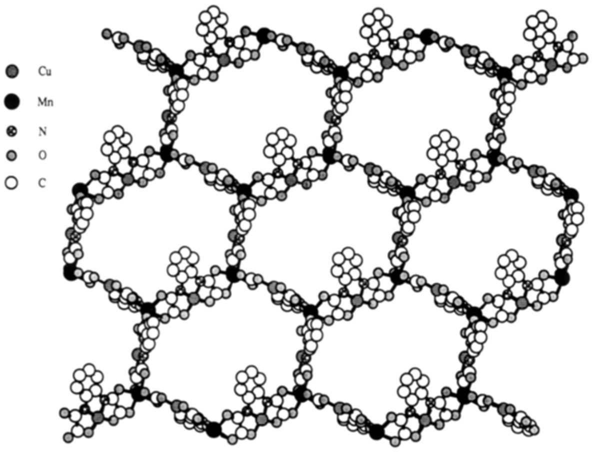

Figure 1. View of a layer in the $(cat)_2Mn_2[Cu(opba)]_3{\cdot}S$ compounds showing the edge-sharing $Mn^{II}_6Cu^{II}_6$ hexagons. The Mn(II) ions are at the corners of the hexagons, and the Cu(II) ions at the middles of the edges (from ref 6).

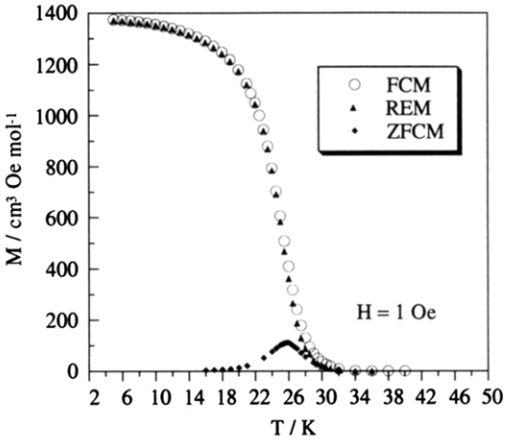

Figure 2. Temperature dependence of the magnetization for $(NBu_4)_2Co_2[Cu(opba)]_3{\cdot}3DMSO{\cdot}3H_2O$ (**1**).

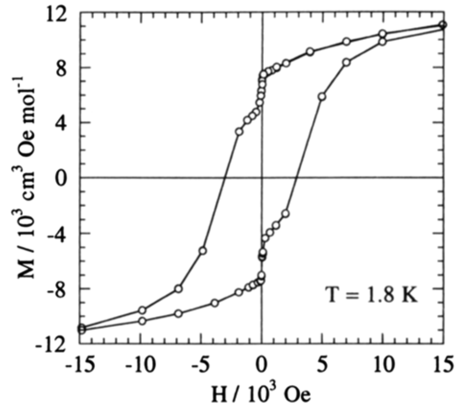

Figure 3. Field dependence of the magnetization for $(NBu_4)_2Co_2[Cu(opba)]_3{\cdot}3DMSO{\cdot}3H_2O$ (**1**).

Replacing Mn(II) with an orbital singlet ground state ($^6A_1$) by Co(II) with an orbital triplet ground state ($^4T_1$) should result in an increase of the coercive field.

Three $(cat)_2Co_2[Cu(opba)]_3{\cdot}S$ molecular-based magnets have been synthesized. Compound **1**, of formula $(NBu_4)_2Co_2[Cu(opba)]_3{\cdot}3DMSO{\cdot}3H_2O$, was prepared by adding 0.075 g (3×10^{-4} mol) of $Co(CH_3CO_2)_2{\cdot}4H_2O$ into a solution of 0.4 g (5×10^{-4} mol) of $(NBu_4)_2Cu(opba)$ in 15 mL of DMSO. The mixture was heated at 50 °C for 15 min and then allowed to stand at room temperature. After 2 days the polycrystalline precipitate was filtered off, washed with DMSO, and dried under vacuum.[9] Warming **1** at 170 °C under vacuum affords compound **2** of formula $(NBu_4)_2Co_2[Cu(opba)]_3{\cdot}2H_2O$.[10] Compound **3**, of formula $(rad)_2Co_2[Cu(opba)]_3{\cdot}0.5DMSO{\cdot}3H_2O$, was synthesized by adding 0.03 g (2.3×10^{-4} mol) of $CoCl_2$ into a solution of 0.33 g (4×10^{-4} mol) of $(rad)_2Cu(opba){\cdot}H_2O$ in 15 mL of DMSO. The mixture was stirred for 30 min. Methanol (25 mL) was then added. The precipitate was isolated by centrifugation, washed with methanol, and dried under vacuum.[11]

Let us first discuss the magnetic properties of **1**. The $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature, shows a minimum at 110 K characterizing a ferrimagnetic behavior.[12] As T is lowered below ca. 35 K, $\chi_M T$ reaches extremely high values and becomes strongly field dependent, which suggests that a magnetic ordering takes place. This is confirmed when studying the temperature dependence of the magnetization (see Figure 2). The field-cooled magnetization (FCM) recorded by cooling within a field of 1 Oe shows a break around $T_c = 32$ K. The remnant magnetization (REM) obtained in turning the field off at 2 K, and warming the sample in zero field is strictly equal to the FCM. All the information induced by the field is retained. The REM vanishes at T_c. The zero-field-cooled magnetization (ZFCM) obtained in cooling down to 2 K in zero field and warming within the field of 1 Oe is extremely weak. Actually, the ZFCM is negligibly small up to ca. 15 K; the magnetic domains are randomly oriented, and the domain walls do not move. The ZFCM slightly increases as T increases above 15 K, due to the thermal agitation which displaces the domain walls. The ZFCM merges with the FCM at T_c. The field dependence of the magnetization, $M = f(H)$, was measured at 1.8 K up to 80 kOe.[13] The most remarkable feature of the M versus H behavior is the hysteresis loop shown in Figure 3, with a coercive field as large as 3000 Oe and a remnant magnetization of ca. 8000 cm^3 Oe mol^{-1}. The shape of this hysteresis loop at low field, although perfectly reproducible, is rather unusual. It might be due to the fact that the sample is a very anisotropic powder. Perhaps also a magnetic aftereffect is operative.[14]

Much the same results are obtained with **2**, except that T_c is equal to 34 K. As for **3**, T_c is also equal to 34 K.[15]

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(9) $(NBu_4)_2Cu(opba)$ was prepared as described in ref 5. Anal. Calcd for $C_{68}H_{108}N_8O_{24}S_3Cu_3Co_2$ (**1**): C, 44.72; H, 5.91; N, 6.14; S, 5.27; Cu, 10.44; Co, 6.45. Found: C, 43.86; H, 5.83; N, 6.18; S, 5.35; Cu, 10.21; Co, 6.40.

(10) Anal. Calcd for $C_{62}H_{88}N_8O_{20}Cu_3Co_2$ (**2**): C, 47.31; H, 5.59; N, 7.12; Cu, 12.11; Co, 7.49. Found: C, 47.39; H, 5.44; N, 7.15; Cu, 12.13; Co, 7.49.

(11) $(rad)_2Cu(opba){\cdot}H_2O$ was prepared as described in ref 6. Anal. Calcd for $C_{57}H_{59}N_{12}O_{26}S_{0.5}Cu_3Co_2$ (**3**): C, 41.63; H, 3.59; N, 10.22; S, 0.97; Cu, 11.59; Co, 7.17. Found: C, 42.03; H, 3.73; N, 10.25; S, 0.94; Cu, 11.25; Co, 6.78.

(12) $\chi_M T$ is equal to 5.9 cm^3 K mol^{-1} at 294 K and 4.9 cm^3 K mol^{-1} at 110 K. The $\chi_M T$ versus T curve for **1** is given in Figure S1 (supplementary material).

(13) The $M = f(H)$ curve for **1** shown in Figure S2 (supplementary material) is characteristic of a powder magnet with a large magnetic anisotropy. The easy magnetization axes of the microcrystallites are randomly oriented with respect to the field direction, and even at 80 kOe the Co(II) magnetic moments are not totally aligned along the field direction. The M versus H curve for **2** is very similar to that for **1**.

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(15) The M versus T curves for **2** and **3** are shown in Figures S3 and S4 (supplementary material), respectively. The M versus H curve for **3** is represented in Figure S5 (supplementary material).

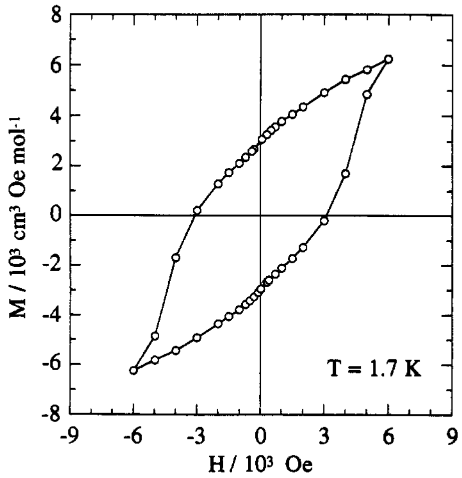

Figure 4. Field dependence of the magnetization for $(rad)_2Co_2[Cu(opba)]_3\cdot0.5DMSO\cdot3H_2O$ (**3**).

The hysteresis loop for **3** (see Figure 4) is more classical. It shows a coercive field of 3100 Oe at 1.7 K. The presence of a third kind of spin carriers in **3**, the organic radicals, does not lead to an increase of T_c, which is in line with what was already observed for the $(cat)_2Mn_2[Cu(opba)]_3\cdot S$ compounds.[5,6]

For the three compounds **1**–**3**, T_c is significantly higher than for the related Mn(II)-containing derivatives. The most striking difference between Co(II) and Mn(II) derivatives, however, concerns the magnitude of the coercivity. The Mn(II) compounds are soft magnets, while the Co(II) compounds exhibit a large coercivity. It is worth emphasizing that if the critical temperatures for the compounds **1**–**3** are still low, the coercivities are much higher than those of Fe_2O_3 or CrO_2.

Our findings strongly suggest that the key requirement to obtain a molecular-based magnet exhibiting a large cooercivity is to incorporate magnetic centers with unquenched orbital momentum in the structure. Coercive fields larger than 1000 Oe were already reported in molecular materials containing low-spin Fe(III) in D_{5h} symmetry ($^2E_{2g}$ ground state),[16] low-spin Mn(III) again in D_{5h} symmetry ($^3E_{2g}$ ground state),[17,18] or high-spin Fe(II) in octahedral symmetry ($^5T_{2g}$ ground state).[19] In all the cases the spin carriers possess a first-order orbital momentum. On the contrary, our work suggests that the purely organic magnets[20,21] with very isotropic spin carriers cannot display significant coercivities. Perhaps, one of the best approaches is to use both organic radicals and anisotropic metal ions as spin carriers.[2,22]

Supplementary Material Available: Figures S1–S5 representing the χ_MT versus T plot for **1**, the M versus H curve at 1.8 K up to 80 kOe for **1**, the M versus T curves with FCM, REM, and ZFCM for **2** and **3**, and the M versus H curve at 1.7 K up to 80 kOe for **3** (5 pages). Ordering information is given on any current masthead page.

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