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Crystal structure and magnetic properties of $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 2(PhCO_2H)$: Evidence of domain formation with different blocking temperatures

Keiji Takeda and Kunio Awaga*
Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

Tamotsu Inabe
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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We studied the crystal structures and magnetic properties of the solvated Mn_{12} benzoate cluster, $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 2PhCO_2H$. This crystal includes nonparallel molecular-plane orientations in the unit cell. The single crystal magnetization curve at 1.7 K shows a hysteresis loop that is very unusual in shape. The curve can be well understood, assuming the following about two domains: that magnetization rotation is frozen in one of the two and is not in the other. This two domain model can also consistently explain the temperature dependence of the ac susceptibility. [S0163-1829(98)50418-3]

Twelve-nuclei manganese complexes have attracted a great deal of interest in the field of molecular magnetism, because of their unusual magnetic properties. They possess a high spin ground state of $S=9-10$ due to an antiferromagnetic interaction between the eight Mn^{3+} $(S=2)$ ions and the four Mn^{4+} $(S=\frac{3}{2})$ ions in the cluster molecule.[1,2] This high spin multiplicity and a strong uniaxial magnetic anisotropy lead to a potential barrier between the up- and down-spin states. At low temperatures, the rotation of the magnetic moments is not free and the friction that accompanies it results in a hysteresis loop of the magnetization curve and in the generation of the imaginary component of ac magnetic susceptibility. A characteristic feature of this component is that the temperature dependence exhibits two maximums in intensity; the reason for this is as yet unknown.

While the crystal structure and the magnetic properties of a Mn_{12} cluster with benzoate ligands, i.e., $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]$ (crystal 1), were reported by R. Sessoli *et al.*,[1] we obtained another form of crystal 1 that included benzoic acids as a crystal solvent, i.e., $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 2(C_6H_5CO_2H)$ (crystal 2). In this paper, we will describe the crystal structure and magnetic properties of crystal 2. We will show convincing evidence for presence of two domains in which the clusters possess different blocking temperatures. We will also analyze the cause of the double maximum feature of the imaginary component of ac susceptibility.

Crystal 2 was prepared by following the procedure in Ref. 1 (Method B). By repeating crystallization with an excess amount of $PhCO_2H$, black block-type crystals were obtained in a yield of ~30%.

Complex crystal 2 crystallizes in the orthorhombic space group $Fdd2$,[3] where one half of the $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 2PhCO_2H$ unit is crystallographically independent. The structure of the Mn_{12} cluster is very similar in many respects to that of nonsolvated form crystal 1. There is a central $Mn_4^{IV}O_4$ cubane that is held within a nonplanar ring of eight Mn^{III} atoms by eight μ_3-O atoms. Peripheral ligation by 16 benzoate and four H_2O groups is exactly the same as those in crystal 1. The crystal solvent (benzoic acid) is connected with the oxygen atoms of H_2O and that of benzoate in the Mn_{12} cluster by hydrogen bonds. Figure 1 shows a projection of the unit cell of crystal 2 along the c axis. The molecular planes are nearly parallel to the c axis, but there are two kinds of molecular-plane orientations with respect to the a or b axis. The dihedral angle between the two planes of different orientation is ~80°. Complex crystal 2 characteristically has a unit cell that includes nonparallel molecular-plane orientations, while the molecular planes are aligned parallel in most of the crystals of the Mn_{12} clusters that have been analyzed to date.[1,2,4] The Mn_{12} cluster has a strong uniaxial magnetic anisotropy (the easy axis is parallel to the molecular one), but it is predicted that the magnetic properties of crystal 2 are almost isotropic in the ab plane.

We measured the temperature dependence of the real χ' and imaginary χ'' components of the ac magnetic susceptibility of crystal 2 using the single crystal at various frequencies. We found that by rotating the crystal, the magnetization became the largest in the field that was parallel to the b axis. The values of $\chi' T$ and χ'' in the field parallel to the b axis

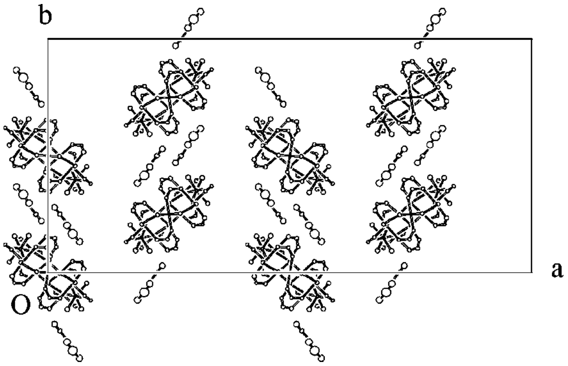

FIG. 1. The projection of the unit cell of crystal 2 along the c axis. The phenyl rings in the benzoates are omitted for the sake of clarity.

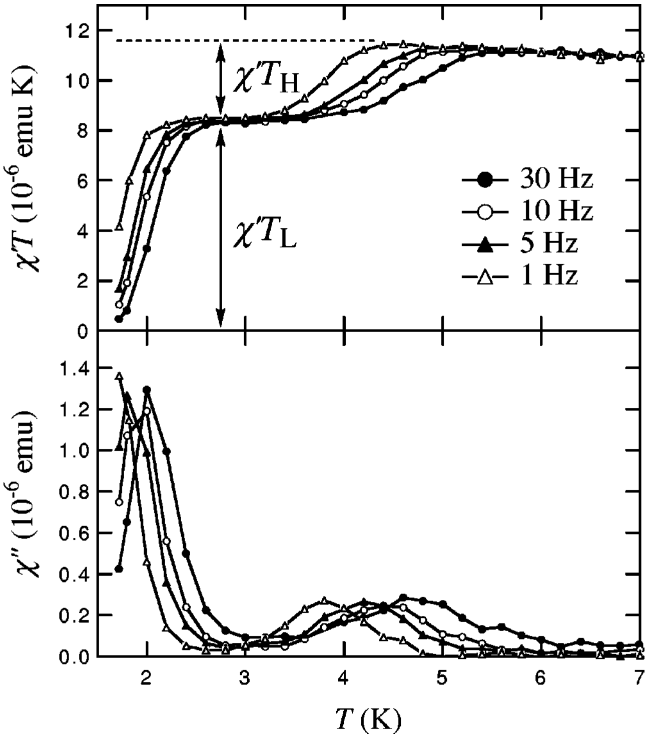

FIG. 2. Temperature dependence of the ac magnetic susceptibility for a single crystal of crystal 2 at various frequencies; (a) plot of $\chi' T$ vs T, where χ' is the real component, (b) plot of χ'' vs T, where χ'' is the imaginary component.

are plotted in Figs. 2(a) and 2(b), respectively, as a function of temperature. Their quantities are for the piece of the crystal. There is a relatively constant value of $\chi' T = 1.13 \times 10^{-5}$ emu K above 5 K. Below this temperature, the value decreases to zero, passing through a plateau ($\chi' T = 8.5 \times 10^{-6}$ emu K) in the range 2.5–3.5 K. In accordance with the rapid decreases in $\chi' T$, the χ'' plots reach two maximums at 2.0 and 4.5 K. As was mentioned previously, the Mn_{12} clusters characterized so far exhibited two maximums of χ'',[2] but there was usually a large difference in intensity between the two peaks. For crystal 2, however, the intensities of the two χ'' maximums are in the same order of magnitude, and the amounts of the changes in $\chi' T$ below and above the plateau are also in the same order of magnitude. We analyzed the systematic frequency dependence of the two χ'' maximums with the equation $\tau = \tau_0 \exp(\Delta E / k_B T)$, where τ_0 is the prefactor, ΔE is the potential barrier, and k_B is the Boltzmann constant. The obtained parameters were $\tau_0 = 3.2 \times 10^{-11}$ s and $\Delta E / k_B = 38$ K for the χ'' maximum at ~ 2 K, and $\tau_0 = 4.7 \times 10^{-9}$ s and $\Delta E / k_B = 66$ K for the χ'' maximum at ~ 4.5 K. We calculated the two kinds of blocking temperatures T_B to be 1.3 and 2.7 K for the χ'' maximums of the lower and higher temperatures, respectively. The analytical method used has been described in detail elsewhere.[5,6] It is worth noting that the value of the $\chi' T$ plateau and the ratio of the χ'' peak heights are significantly sample dependent. In spite of this, we always obtained almost the same values of τ_0, ΔE, and T_B for the two peaks in χ''.

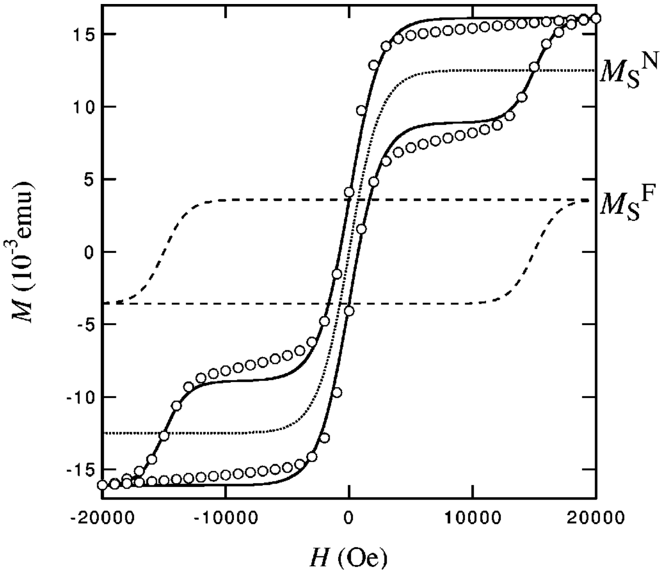

FIG. 3. Magnetization curve of a single crystal of crystal 2 at 1.7 K under the field that is parallel to the b axis. The solid curve is a theoretical fit of the two domain model. The broken and dotted curves represent the contributions of the frozen and nonfrozen domain, respectively.

Figure 3 shows the magnetization curve of the single crystal of crystal 2 at 1.7 K that was used for the ac magnetic susceptibility measurements. The measurements were performed in the field parallel to the b axis. The curve exhibits a hysteresis loop as well as the other Mn_{12} clusters; the shape, however, is very unusual. As the field is increased from -20 to 0 kOe, the magnetization is almost constant. When the field changes in sign, it shows a rapid increase and reaches a plateau between 5 and 15 kOe. Above 15 kOe, the magnetization rapidly increases again and is saturated. When the field is decreased from 20 kOe, the same behavior can be seen. The sudden changes in magnetization at 0 and ± 15 kOe cannot be explained as a quantum tunneling of magnetization,[7–10] because the step fields (± 15 kOe) are significantly temperature dependent and because polycrystalline samples also exhibit similar behavior (not shown). Other researchers have also found similar types of magnetization curves for $[Mn_{12}O_{12}(O_2CMe)_4(O_2CEt)_{12}(H_2O)_4] \cdot 2H_2O \cdot 4EtCO_2H$[11] and $[Mn_{12}O_{12}(O_2CC_6H_4Me\text{-}4)_{16}(H_2O)_4] \cdot HO_2CC_6H_4Me\text{-}4$.[12]

The key to understanding the unusual magnetization curve of crystal 2 is that the measurement temperature (1.7 K) is just between the two T_B, which were estimated in the ac susceptibility measurements. We found that the magnetization curve can be well interpreted, assuming the presence of two domains at 1.7 K: the rotation of magnetization is frozen in the domain of $T_B = 2.7$ K and it is not in that of $T_B = 1.3$ K. Since it is difficult to theoretically express the magnetization curves of the two phases, we used the phenomenological equations, $M_F = M_s^F [1 - \exp\{-2A(H \pm H_0)\}] / [1 + \exp\{-2A(H \pm H_0)\}]$ and $M_N = M_s^N \{1 - \exp(2BH)\} / \{1 + \exp(2BH)\}$ for the frozen and non-frozen domains, respectively. In the equations, M_s^F and M_s^N correspond to the saturation magnetization of the two domains which could be proportional to their sizes. The other parameters (A, B, and H_0) only explain the curvature. The solid curve that can be fitted to the experimental plots in Fig. 3 is the theoretical one of $M=M_F+M_N$ with $M_s^F=3.56\times10^{-3}$ emu, $M_s^N=1.25\times10^{-2}$ emu, $H_0=15$ kOe, $A=5.2\times10^{-4}$, and $B=4.0\times10^{-4}$. The broken and dotted curves in the figure show the behavior of the components, M_F and M_N, respectively. One can see that the magnetization curve is well explained by the sum of the two contributions. In addition, it is significant that the ratio $M_s^F/M_s^N=0.28$ almost completely agrees with the ratio of the $\chi' T$ changes below and above the plateau, i.e., $\chi' T_H/\chi' T_L=0.33$ [the definitions of $\chi' T_H$ and $\chi' T_L$ are shown in Fig. 2(a)]. The ratio was strongly sample dependent, but the relationship $M_s^F/M_s^N=\chi' T_H/\chi' T_L$ always existed as a unique value for the crystal.

We confirmed that the magnetic properties of crystal 2 were almost isotropic in the ab plane, although the magnetization along b axis was slightly larger than that along the a axis. The magnetization along the c axis was much smaller than those along the a and b axes. In addition, the magnetization curve in the field parallel to the c axis exhibited linear field dependence at least up to 20 kOe, without hysteresis. The temperature dependence of the χ'' component of the ac susceptibility along the c axis was always zero in the entire temperature range of 1.7–7 K. The above is consistent with the well-known fact that the magnetic hard axis of the Mn_{12} cluster is parallel to the molecular plane.

We proposed domain formation in the crystal of crystal 2, in which the Mn_{12} clusters possess different potential barriers or blocking temperatures. The ΔE value of one domain is almost double that of the other one. The domain formation mechanism is unclear, however, it is notable that another Mn_{12} material which also exhibited an unusual magnetization curve of the type of crystal 2, also included a nonparallel molecular-plane alignment in its crystal.[13] When the flat Mn_{12} clusters are all aligned parallel on the same plane, the dipole fields of the neighbors must enhance the uniaxial magnetic anisotropy of the cluster, making the blocking temperature higher. The parallel molecular-plane alignments may stabilize the domain of high T_B. In a nonuniaxial crystal with respect to magnetic anisotropy, because of a nonparallel molecular orientation, on the other hand, the anisotropy may be less stable than in the uniaxial crystals, resulting in the occurrence of the two domains. Detailed magnetic measurements on a single crystal of crystal 2 are in progress, changing the thermal history of the samples and so on.

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[3] Crystal data: C126H98O25Mn12, $M=3103.41$, orthorhombic, $Fdd2$, $a=56.21(3)$, $b=27.12(2)$, $c=16.970(10)$ Å, $V=25\,871(23)$ Å^3, $Z=8$, $D_c=1.593$ g cm^{-3}, μ(Mo-Kα) $=11.62$ cm^{-1}, $T=-123\,°$C, $3\leqslant 2\theta\leqslant 55°$, $R(R_w)=0.088(0.104)$ for 3903 unique reflections with $F>3\sigma(F)$.

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