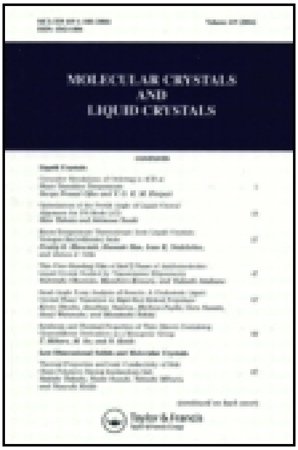

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Magnetic Properties of Molecular Compounds of $Mn_{12}Ph$

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Magnetic Properties of Molecular Compounds of $Mn_{12}Ph$

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We report the magnetic properties of two kinds of new molecular compounds of $Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4$ (abbreviated as $Mn_{12}Ph$). (i) The salt of *m*-N-methylpyridinium nitronylnitroxide (abbreviated as *m*-MPYNN$^+$) and $[Mn_{12}Ph]^-$ was prepared. The EPR spectra of (*m*-MPYNN$^+$)$[Mn_{12}Ph]^-$ are composed of two separate absorptions of *m*-MPYNN$^+$ and $[Mn_{12}Ph]^-$, indicating that the exchange interaction between them is negligibly weak. In spite of the weak interaction, the magnetic relaxation in $[Mn_{12}Ph]^-$ is significantly enhanced in the salt. (ii) The crystal structure and magnetic properties of a solvated $Mn_{12}Ph$, *$[Mn_{12}Ph]$•$2PhCO_2H$, were studied. The crystal includes non-parallel molecular-plane orien*tations in the unit cell. The single-crystal magnetization curve at 1.7 K shows a hysteresis loop that is very unusual in shape. It is found that the curve can be well understood, assuming the presence of two domains : the magnetization rotation is frozen in one of the two and is not in the other.

Keywords: Mn_{12} clusters; organic radical; molecular compounds; magnetic relaxation

ENHANCEMENT OF MAGNETIC RELAXATION IN (*m*-MPYNN$^+$)$[Mn_{12}Ph]^-$ (ref. [1])

Twelve-nuclei manganese complexes have attracted a great deal of interest in the field of molecular magnetism, because of its unusual magnetic properties. The materials 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=3/2) ions in the cluster molecule. 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[2-5]. While these properties are considered to originate in the single cluster molecule, it is interesting to see how they are affected by the environment around the Mn_{12} cluster. In addition, since the nanoscale magnetic materials are also attracting interest as a building block of more unusual magnetic materials, it is important to elucidate their intermolecular interactions.

Materials

A stable organic radical family, nitronylnitroxide, has been studied extensively, because of its potential ferromagnetic interactions[6]. The materials are so stable that it is easy to produce ionic nitronylnitroxides by putting a cationic or anionic moiety on the α-carbon. In this work, we prepared a hybrid salt of the *m*-*N*-methylpyridinium nitronylnitroxide (abbreviated as *m*-$MPYNN^+$) cation and the $[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]^-$ (abbreviated as $[Mn_{12}Ph]^-$) anion. The crystalline sample of (m-$MPYNN^+$)$[Mn_{12}Ph]^-$ was obtained by the following reaction; m-MPYNN•I + $Mn_{12}Ph \rightarrow$ (m-$MPYNN^+$)$[Mn_{12}Ph]^-$ +

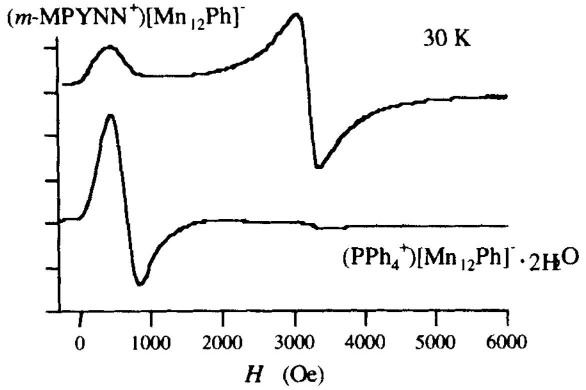

FIGURE 1 EPR spectra of $(PPh_4^+)[Mn_{12}Ph]^- \cdot 2H_2O$ and (m-$MPYNN^+$)$[Mn_{12}Ph]^-$ at 30 K

(1/2)I_2. However, the crystals were unstable probably due to evaporation of crystal solvents and became mosaic quickly.

EPR Spectroscopy

The temperature-variable X-band EPR measurements were performed on (*m*-MPYNN$^+$)[Mn_{12}Ph]$^-$ and a reference sample (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ in the temperature range 7-300 K. Their spectra at 30 K are shown in Fig. 1. (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ exhibits an absorption below ca. 80 K at g=10.5 which is assigned to that of [Mn_{12}Ph]$^-$. (*m*-MPYNN$^+$)[Mn_{12}Ph]$^-$ exhibits two absorptions at g=10.5 and g=2, which are ascribed to [Mn_{12}Ph]$^-$ and *m*-MPYNN$^+$, respectively. The separation of the EPR absorptions of the two species indicates that the exchange interaction between *m*-MPYNN$^+$ and [Mn_{12}Ph]$^-$ is not significant, while the spectrum clearly shows an overlap between the absorption tails and suggests a cross-relaxation process.

DC Magnetization and AC Magnetic Susceptibility

The magnetization curves of (*m*-MPYNN$^+$)[Mn_{12}Ph]$^-$ and (PPh_4^+)[Mn_{12}Ph]$^-$ •$2H_2O$ were examined at 1.7 K in the field up to 2 T. The results are shown in Fig. 2. The open circles in this figure show the magnetization curve for (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$. The plots make a large hysteresis loop whose

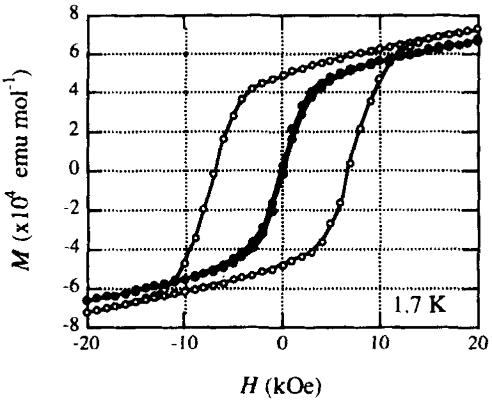

FIGURE 2 The magnetization curves of (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ (open circle) and (*m*-MPYNN$^+$)[Mn_{12}Ph]$^-$ (closed circle) at 1.7 K.

coercive field is about 7000 Oe. The closed circles represent the results on (m-MPYNN$^+$)[Mn_{12}Ph]$^-$. Surprisingly the loop almost disappears and the coercive field is less than 100 G which is smaller than that of (PPh_4^+)[Mn_{12}Ph]$^-$ •$2H_2O$ by two orders of magnitude. The disappearance of the loop means that the magnetic relaxation in the Mn_{12} cluster is seriously enhanced in (m-MPYNN$^+$)[Mn_{12}Ph]$^-$.

The ac magnetic susceptibilities were recorded for the polycrystalline samples of (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ and (m-MPYNN$^+$)[Mn_{12}Ph]$^-$ in the temperature range 1.7-8 K. The temperature dependences of the imaginary components χ'' for the two salts are shown in Fig. 3. The values of χ'' for (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ in Fig. 3(a) make a maximum at 4 K, with systematic frequency dependence. This can be attributed to a freezing process of the magnetization: as the temperature is decreased, the thermal energy is reduced to a point where the magnetic moment (magnetization) of the Mn_{12} cluster cannot follow the oscillating field and brings about the imaginary component of the ac susceptibility. And when the temperature is decreased more, the motion of the magnetic moment is frozen and the value of χ'' becomes small. By examining the frequency dependence of χ'', T_B for (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ is calculated to be 2.7 K. The behavior of the ac susceptibility is quite consistent with the large hysteresis loop of the magnetization curve in Fig. 2 that was measured below T_B. The Mn_{12} clusters are known to exhibit two maximums in χ'', although the reason for them has not been given yet. Actually we found another small maximum in χ'' at ca. 2 K (see the inset of Fig. 3(a)).

Figure 3(b) shows the temperature dependence of χ'' for (m-MPYNN$^+$)[Mn_{12}Ph]$^-$. The values of χ'' make a main peak at 2 K, while a small maximum appears at 3 K (see the inset of Fig. 3(b)). Since the bulk behavior is governed by the relaxation process which exhibits the main peak in χ'', T_B for (m-MPYNN$^+$)[Mn_{12}Ph]$^-$ is calculated to be 1.0 K, using the data around 2 K. This is also consistent with the very small hysteresis loop of the magnetization at 1.7 K.

The values of T_B for (PPh_4^+)[Mn_{12}Ph]$^-$•$2H_2O$ and (m-MPYNN$^+$)[Mn_{12}Ph]$^-$ are 2.7 K and 1.0 K, respectively. The crucial difference in the magnetization curve at 1.7 K between them can be simply understood by the low-temperature shift of T_B in (m-MPYNN$^+$)[Mn_{12}Ph]$^-$. However, it is worth noting here that the low-temperature shift of T_B is brought about, not by the simple low-temperature shift of the main maximum in χ", but by the intensity switch between the higher- and lower-temperature maximums in χ". It must be a future problem to clear the microscopic origin of the two maximums.

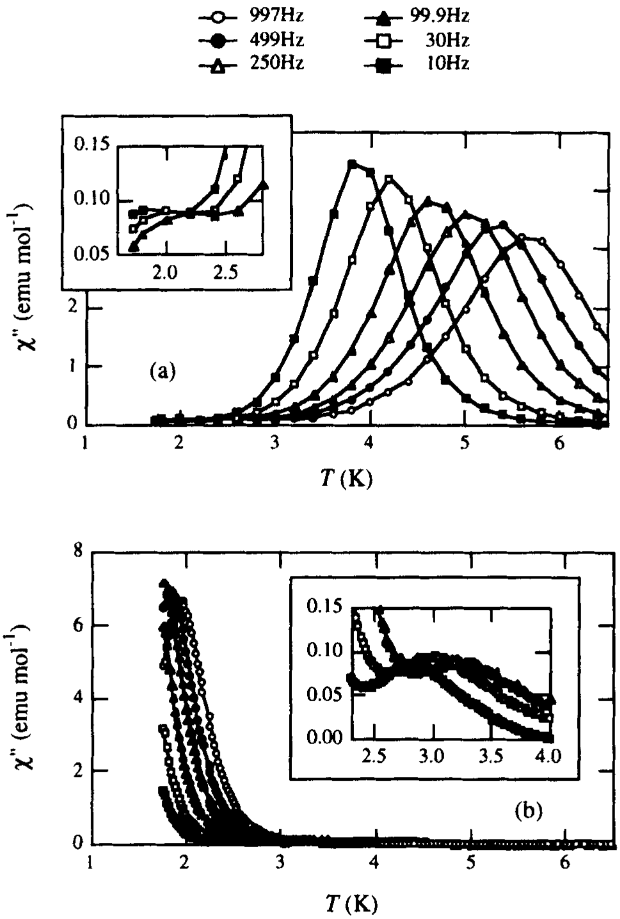

FIGURE 3 Temperature and frequency dependence of χ" for $(PPh_4^+)[Mn_{12}Ph]^- \cdot 2H_2O$ (a) and $(m\text{-MPYNN}^+)[Mn_{12}Ph]^-$ (b).

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $[Mn_{12}Ph]\bullet 2PhCO_2H$ (ref. [6])

While the crystal structure and the magnetic properties of $Mn_{12}Ph$ were reported by R. Sessoli et. al.[4] , we obtained another form of $Mn_{12}Ph$ that included benzoic acids as a crystal solvent, i.e. $[Mn_{12}Ph]\bullet 2PhCO_2H$. In this section, we describe the crystal structure and magnetic properties of $[Mn_{12}Ph]\bullet 2PhCO_2H$. We show convincing evidence for presence of two domains in which the clusters possess different blocking temperatures.

Sample Preparation and Crystal Structure

$Mn_{12}Ph$ was prepared by the procedure in ref. [4] (Method B). By repeating crystallization with an excess amount of $PhCO_2H$, black block-type crystals of $[Mn_{12}Ph]\bullet 2PhCO_2H$ were obtained in a yield of ~30%.

Complex $[Mn_{12}Ph]\bullet 2PhCO_2H$ crystallizes in the orthorhombic space group F_{dd2}, where a half of the $[Mn_{12}Ph]\bullet 2PhCO_2H$ unit is crystallographically independent. The structure of the Mn_{12} cluster is very similar in many

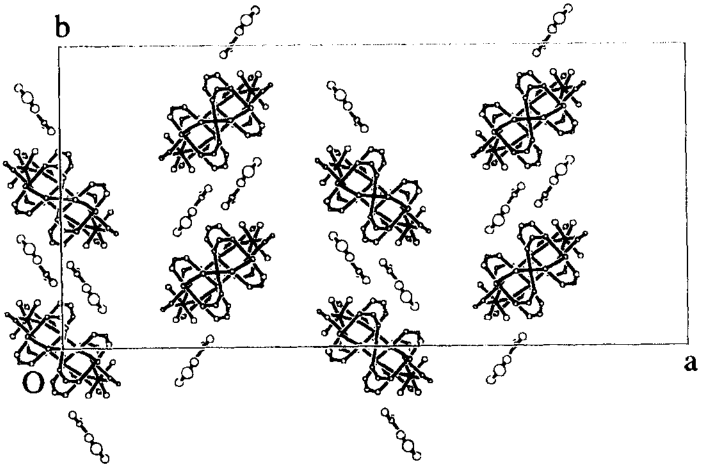

FIGURE 4 Projection of the crystal structure of $[Mn_{12}Ph]\bullet 2PhCO_2H$ along the *c* axis.

respects to that of the non-solvated form. There is a central $Mn^{IV}{}_4O_4$ cubane that is held within a nonplanar ring of eight Mn^{3+} atoms by eight μ_3-O atoms. Peripheral ligation by sixteen benzoate and four H_2O is exactly the same as those in the non-solvated form. The crystal solvent (benzoic acid) is connected with the hydrogen of H_2O and the oxygen of benzoate in the Mn_{12} cluster by hydrogen bonds. Figure 4 shows a projection of the unit cell of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ 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 ca. 80°. $[Mn_{12}Ph]{\bullet}2PhCO_2H$ characteristically has a unit cell that includes non-parallel 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[4,5,8]. The Mn_{12} cluster has a strong uniaxial magnetic anisotropy (The easy axis is parallel to the molecular axis), but it is predicted that the magnetic properties of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ are almost isotropic in the *ab* plane.

Magnetic Properties

We measured the temperature dependence of the ac magnetic susceptibility for $[Mn_{12}Ph]{\bullet}2PhCO_2H$ using a single crystal at various frequencies. The values of χ'' in the field parallel to the *a* axis are plotted in Fig. 5, as a function of temperature. 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 in χ''[5], but there were usually a large difference in intensity between the two peaks. For $[Mn_{12}Ph]{\bullet}2PhCO_2H$, however, the intensities of the two χ'' maximums are in the same order of magnitude. By analyzing the frequency dependence of χ'' for the higher-temperature and lower-temperature maximums, T_B can be calculated to be 2.7 and 1.3 K, respectively.

Figure 6 shows the magnetization curve for the single crystal of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ at 1.7 K that was used for the ac magnetic susceptibility measurements. The measurements were performed in the field parallel to the *a* 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

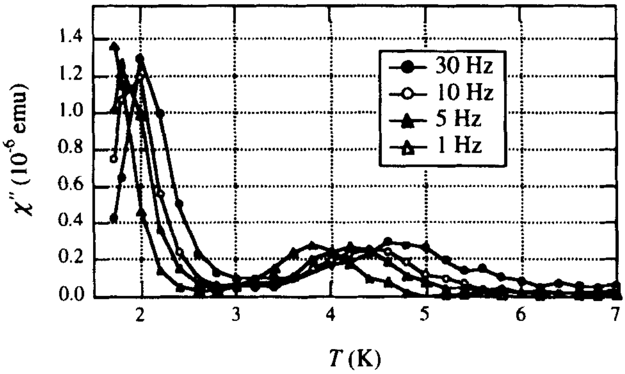

FIGURE 5 Temperature and frequency dependence of χ" for a single crystal of $[Mn_{12}Ph]\cdot 2PhCO_2H$.

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[9], because the step fields (±15 kOe) are significantly temperature dependent and because polycrystalline samples also exhibit similar behavior (not shown). The key to understanding the unusual magnetization curve of $[Mn_{12}Ph]\cdot 2PhCO_2H$ 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 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

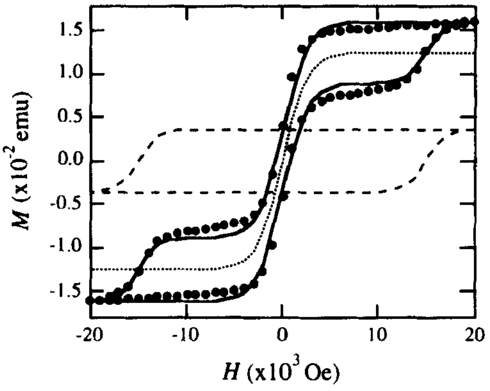

FIGURE 6 The magnetization curve of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ at 1.7 K.

are 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. 5 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 shows 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.

The crystal of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ includes two kinds of the Mn_{12} clusters with different potential barriers or blocking temperatures. That's why the material shows the two maximum in χ''. Detailed magnetic measurements on the single crystal of $[Mn_{12}Ph]{\bullet}2PhCO_2H$ are in progress, changing the thermal history of the samples and so on.

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