

Soluble Single-Molecule Magnet:  $Mn_{12}$ -stearate

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A new polynuclear complex of manganese stearate has been prepared by substitution of acetate with stearic acid. The stearate ion with long alkyl chain was used to isolate molecular  $Mn_{12}$  cluster from each other. The  $Mn_{12}$ -stearate compound prepared is soluble in most organic solvents and resistant against water catalyzed reduction. The  $Mn_{12}$ -stearate compound shows similar electrochemical, magnetic properties to the pristine  $Mn_{12}$ -acetate.

**Keywords :** Magnetic properties,  $Mn_{12}$ , Stearate.

## Introduction

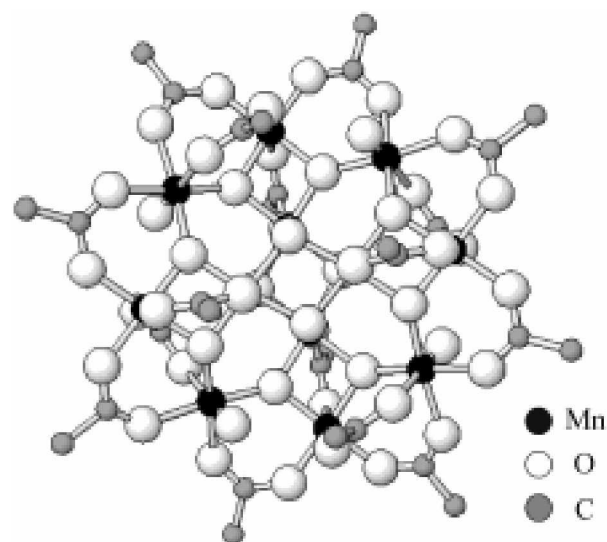
The miniaturization of information storage drives the fabrication for nano-sized magnetic materials, which can be prepared either by fragmentation of bulk ferromagnets or by building up large molecules.<sup>1</sup> Among these materials, the single-molecule magnets (SMMs)<sup>2</sup> are considered as candidates for high-density memory devices because each molecule is well-defined with order of 10-20 Å in diameter and could potentially be used in storing a large density of information.<sup>3</sup> Also understanding the magnetic properties of SMMs is important since the studies link the gap between the quantum and classical magnetic mechanism.<sup>4</sup>

For the SMMs, the source of the magnetic anisotropy arises from the molecules high-spin ground state combined with appreciable zero-field splitting.<sup>5</sup> The magnetic moment of a molecule has two preferred orientations, "up" or "down" relative to the molecule's axial anisotropy axis. When the temperature is much lower than the energy barrier to flip the spin from up to down, the spin of the SMM can be magnetized in one direction. This phenomenon, the magnetic bistability, shows that SMMs can be used as a data storage device.<sup>6</sup> Slow magnetization relaxation is evident, leading to unusual magnetic properties: steps in the magnetization hysteresis loop; frequency-dependent out-of-phase ac magnetic susceptibility signals; a divergence between the zero-field-cooled and field-cooled magnetization at the "blocking" temperature; and slow magnetization decay after an external field is removed below the "blocking temperature".<sup>6</sup>

A few families of molecules have been currently known as SMMs, and the one of most extensively studied SMMs is  $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4] \cdot 4H_2O \cdot 2CH_3COOH$ , commonly called " $Mn_{12}$ -Ac" or simply " $Mn_{12}$ ".  $Mn_{12}$ -Ac, firstly synthesized by Lis,<sup>7</sup> consist of twelve manganese ions in which eight of the Mn in ring are in the +3 oxidation state ( $S=2$ ) and four in cubane are in the +4 state ( $S=3/2$ ), as shown Figure 1. These Mn ions are magnetically coupled to given total  $S=10$  in the ground state.<sup>8a</sup> Hendrickson group and others

have reported many other dodecanuclear manganese complexes which are structurally related, using other carboxylate such as benzoate, propionate, halobenzoate, phenylacetate and *tert*-butylacetate, and the like as ligands.<sup>8</sup> Some  $Mn_{12}$  complexes with one- and two-electron reduced clusters<sup>9</sup> and mixed metal dodecanuclear clusters<sup>10</sup> have been also studied recently. Magnetic properties of  $Mn_{12}$  derivatives have turned out to be dependent on carboxylic acid substituted in the cluster. Multi-layer Langmuir-Blodgett films was also reported using  $Mn_{12}$  SMMs and lipid molecules to design well-organized molecular multilayers.<sup>11</sup>

Most of the reported  $Mn_{12}$ -derivative compounds show slow decomposition presumably due to the oxidation-reduction of  $Mn_{12}O_{12}$  species of the complex in atmospheric environment. This undesirable redox reaction is accelerated by atmospheric oxygen and water. For example,  $Mn_{12}$ -Ac is relatively stable in the solid state but easily decomposed in  $CH_3CN$  solution when the solution is exposed in air. Substitution of bulky ligands results in stabilization of the prepared  $Mn_{12}$  compounds. Also the low solubility of the  $Mn_{12}$  compounds in organic solvents make difficult to select appropri-



**Figure 1.** The structure of  $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]$  ( $Mn_{12}$ -Ac) in *ab* plane.<sup>8</sup> H atoms are omitted.

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ate solvents for thin film of  $Mn_{12}$  compounds as well as to study electrochemical study in various solvents.

In this context, we have chosen a carboxylic acid such as stearic acid ( $CH_3(CH_2)_{16}COOH$ ) to cover  $Mn_{12}$  cluster with bulky alkyl chains to make the molecule hydrophobic. The resulting molecule would have reliable solubility owing to the outside bulky ligands. Herein, we present the synthesis and characterization of a new  $Mn_{12}$  derivative by the substitution of acetate in  $Mn_{12}$  with stearic acid.

### Experimental Section

All chemicals were obtained from Aldrich and used as received.  $Mn_{12}$ -Ac was prepared by the method reported by Lis.<sup>7</sup> Stearic acid (1.1 g, 4.0 mmol) was added to a slurry of  $Mn_{12}$ -Ac (0.5 g, 0.25 mmol) in  $CH_2Cl_2$  (25 mL) and the mixture was stirred overnight. The exchanged free acetic acid was removed together with  $CH_2Cl_2$  under reduced pressure from slurry-solution mixture. The residual powder was dissolved in ether, filtered, and layered with hexane. The layering solution was allowed to stand in low temperature (about  $-5$  °C). Black powder was obtained by filtration, washed with hexane, and then dried in air.

Thermogravimetric analysis (TGA) were conducted on a TA Instruments SDT 2960 in nitrogen atmosphere using a heating rate of  $10$  °C/min from room temperature to  $1200$  °C. Infrared (IR) spectra were obtained in  $3600$  to  $400$   $cm^{-1}$  range by a Nicolet 205 FT-IR spectrometer. The sample was ground with dry KBr and pressed into a transparent disk. Elemental Analysis was performed by CE instruments EA1110 and ICP-MS was performed by VG Elemental PQ2 Turbo at the Inter-University Center of Natural Science Research Facilities in Seoul National University.

Electrochemical studies were performed by a BAS 100W voltammetric analyzer and a standard three-electrode assembly (glassy carbon working, Pt plate auxiliary and Ag/AgCl reference) with  $0.1M$   $NBu_4^+PF_6^-$  as supporting electrolyte. No IR compensation was employed. Quoted potential values are versus the ferrocene/ferrocenium couple measured under the same conditions. The scan rate for cyclic voltammetry and differential pulse voltammetry was set at  $100$  and  $20$  mV, respectively. The concentration of the complexes was approximately  $1$  mM.

Variable temperature direct current (dc) magnetic susceptibility measurements were carried out on a Quantum Design MPMS 7 SQUID magnetometer with an applied magnetic field of  $100$  Gauss in the temperature range of  $2$ - $300$  K. The hysteresis loop data of the  $Mn_{12}$ -stearate were collected at  $2.0$  K.

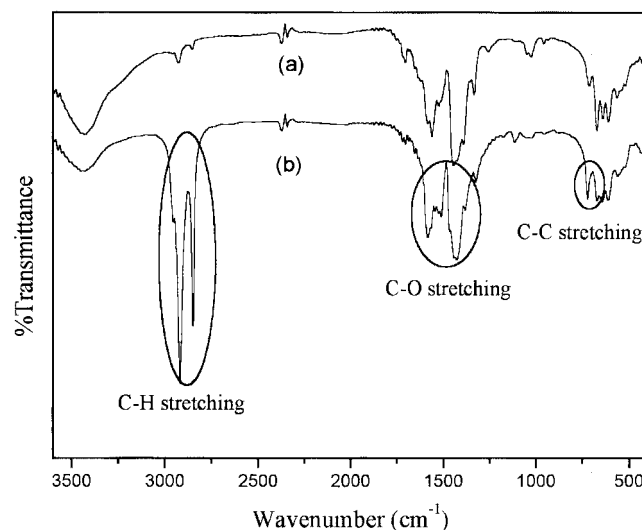
### Result and Discussion

**Synthesis.** The  $Mn_{12}$ -stearate was obtained as an amorphous phase, which was confirmed by powder X-ray diffraction, presumably because the substituted long alkyl chains may strongly disturb the crystallization of  $Mn_{12}$ -stearate.  $Mn_{12}$ -stearate is sticky liquid-like powder and very soluble

in most organic solvents. Reverse reaction was possible through the ligand exchange using excess acetic acid and the crystalline  $Mn_{12}$ -Ac was successfully obtained, which confirms existence of  $Mn_{12}$  moiety in  $Mn_{12}$ -stearate compound prepared in this study.  $Mn_{12}$ -Ac is soluble only in  $CH_3CN$  and is easily decomposed in  $H_2O$  to give brown precipitates. Compared with pristine  $Mn_{12}$ -Ac,  $Mn_{12}$ -stearate is stable in various organic solutions in aerobic condition at least for a month. Powder sample of  $Mn_{12}$ -stearate merely aggregates in  $H_2O$  owing to the strong hydrophobic character of long hydrocarbon chain. Analysis: calculated for  $C_{212}H_{416}Mn_{12}O_{52}$ : C 57.13; H 9.41; Mn 14.79%; found: C 57.52; H 10.00; Mn 15.19%. The suggested chemical formula is  $[Mn_{12}O_{12}(CH_3(CH_2)_{16}CO_2)_{11}(CH_3CO_2)_5(H_2O)_4] \cdot 2CH_3CO_2H$ . The ligand substitution is likely to be incomplete as shown in the chemical analysis, which is attributable to the steric hindrance after the partial substitution of the bulky stearate ligands.

**FT-IR.** The IR spectra of the title compound are shown in Figure 2. The band in the vicinity of  $1700$   $cm^{-1}$  is assigned as  $(OCO)_{asym}$  corresponding to free carboxylic acids, which is ascribed to acetic acids in  $Mn_{12}$ -stearate. On complex formation, this  $(OCO)_{asym}$  band is shifted to a lower frequency, the vicinity of  $1580$   $cm^{-1}$ , which show that complex formation is carried out through the carboxyl group.<sup>12</sup> The band at  $2850$   $cm^{-1}$  is assigned to the C-H stretching. Though the IR spectra of  $Mn_{12}$ -stearate are very similar to that of pristine  $Mn_{12}$ -Ac compound, C-H stretching in the former compound is especially enhanced than that of the latter, which due to the long alkyl chain of stearate ligand. In addition, we assigned the broad bands shown at  $3400$   $cm^{-1}$  to O-H stretching, which are characteristic of hydroxyl group of  $H_2O$  hydrated.

**TG Analysis.** The thermal stability of air-dried  $Mn_{12}$ -stearate was investigated by TGA. In Figure 3, the weight losses at  $150$  °C are about 3.8%, which is ascribed to evaporation of carboxylic acids and water in the prepared  $Mn_{12}$ -stearate. The next weight loss at around  $300$  °C corresponds to decomposition of  $Mn_{12}$ -stearate, giving  $Mn_3O_4$  and car-



**Figure 2.** The FT-IR spectra of  $Mn_{12}$ -Ac(a) and  $Mn_{12}$ -stearate(b).

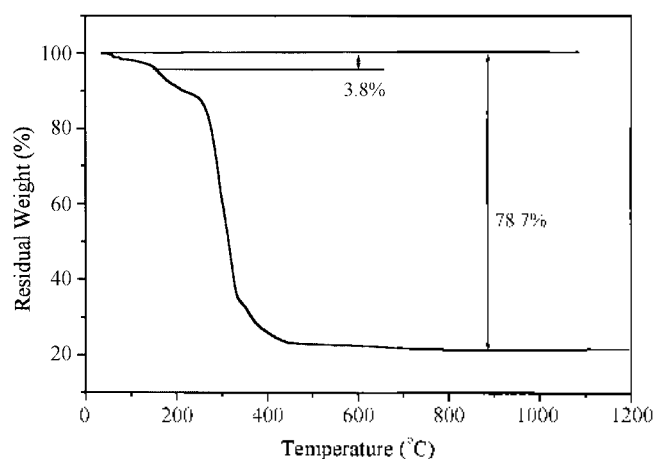


Figure 3. TGA of  $Mn_{12}$ -stearate under  $N_2$  flowing.

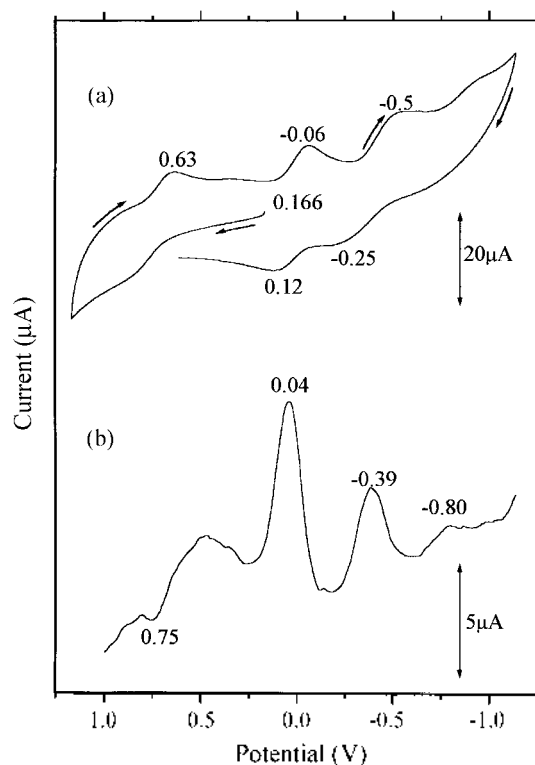


Figure 4. (a) The CV and (b) the DPV data of  $Mn_{12}$ -stearate.

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**Electrochemistry.** Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) provide electrochemical properties and characteristics of the prepared compound and also give insight into any complicating side processes such as pre- and post-electron-transfer reaction as well as kinetic considerations. In Figure 4, the CV and DPV data for  $Mn_{12}$ -stearate in  $CH_2Cl_2$  solution is plotted. There are several redox couples apparent, three on the reduction side and one on the oxidation side. One of these redox couples appear to be reversible or quasi-reversible, the first reduction process at 0.04 V. For this one, the forward and reverse waves are well formed with a peak separation (180 mV) comparable to

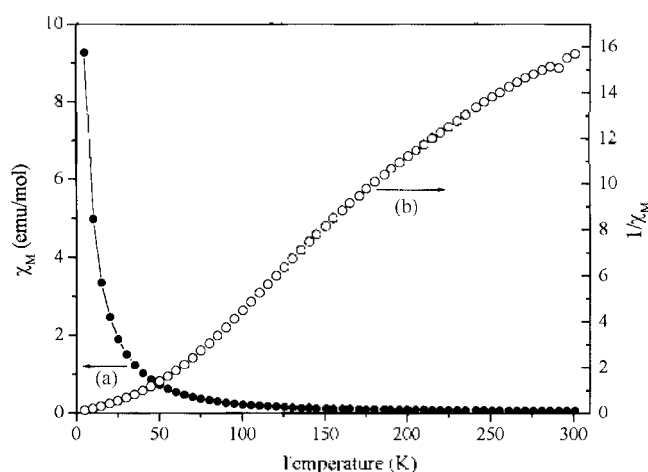
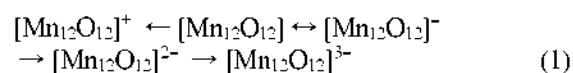


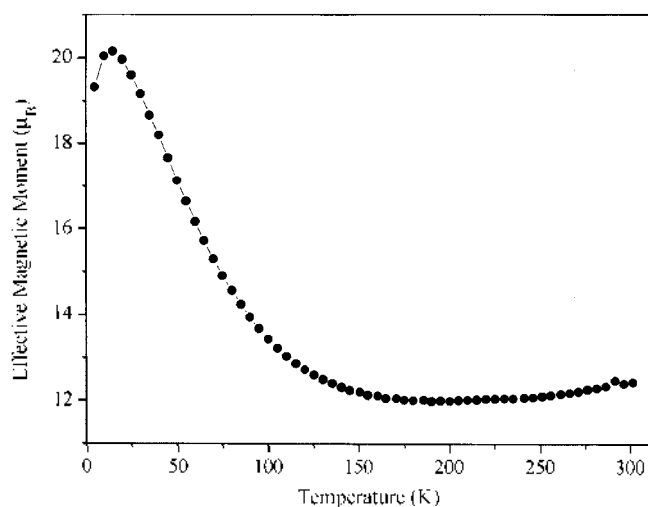
Figure 5. (a) Magnetic susceptibility of  $Mn_{12}$ -stearate, (b) reciprocal magnetic susceptibility  $\chi_M$  versus temperature of  $Mn_{12}$ -stearate at 100 Gauss.

that of ferrocene under the same conditions.

The peak separation for other redox couples, the second and third reduction, and the first oxidation, is much larger than that for the first reduction. These oxidations and reductions appear to be electrochemically irreversible, a conclusion supported by the DPV scan that show broader, ill-formed peaks in contrast to the sharper, better-formed peak for the first reduction. Hendrickson *et al.* reported that the potentials of the first oxidation and reduction waves depend on the response to the electronic properties of the carboxylate, and the electronegative carboxylate causes to reduce the electron density on the metal cluster and thereby makes the cluster easier to be reduced and harder to be oxidized.<sup>8d</sup> The first oxidation and reduction for  $Mn_{12}$ -stearate were observed at 0.75V and 0.04V, respectively. Our electrochemical study shows that the first oxidation and reduction for  $Mn_{12}$ -Ac were 0.80V and 0.21V, similar to those values (0.82V and 0.19V) reported by Hendrickson *et al.*<sup>8c</sup> The long alkyl chains in stearate make the cluster difficult to be reduced and facile to be oxidized compared with  $Mn_{12}$ -Ac. An electron donating substituent of stearate causes the carboxylate to become more basic, enhancing the electron density on the metal cluster. It should be also noted that for the  $Mn_{12}$ -stearate the first oxidation was irreversible and the second oxidation was not observed in the CV and DPV measurements. The electrochemical results may be summarized by eq. 1.



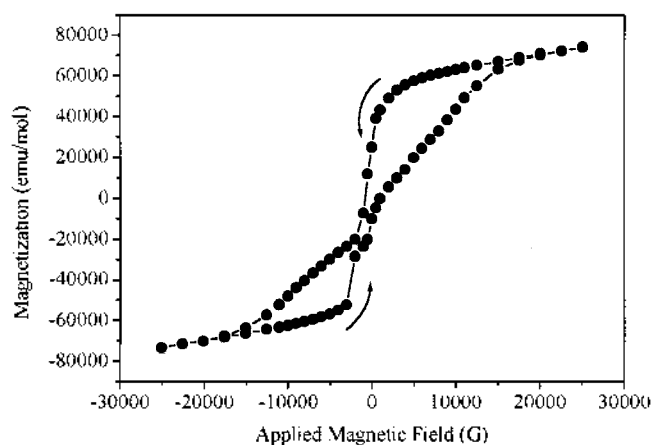
**Magnetic Properties.** Variable-temperature dc magnetic susceptibility data were collected for  $Mn_{12}$ -stearate in an applied magnetic field of 100 G. Figure 5(a) shows that the  $\chi_M$  increases in low temperature, presenting paramagnetic behavior of the complex. In Figure 5(b), the reciprocal value of  $\chi_M$  is close to zero in low temperature, which indicates that the magnetic interaction of  $Mn_{12}$ -stearate is likely to



**Figure 6.** Effective magnetic moments of  $Mn_{12}$ -stearate.

involve ferromagnetic characteristics. In Figure 6, effective magnetic moment ( $\mu_{eff}$ ) versus temperature is shown. From this plot, it is seen that  $\mu_{eff}$  drops slightly from  $12.3 \mu_B$  at 300 K to  $12.0 \mu_B$  at 190 K, then it steadily increases with decreasing temperature to reach a maximum of  $20.1 \mu_B$  at 15.0 K, below which it drops again sharply to  $19.3 \mu_B$  at 5 K. If there is no magnetic exchange interaction in a  $Mn_4^{IV}Mn_8^{III}$  complex, the spin only effective magnetic moment with  $g=2.0$  should be  $\mu_{eff}=15.9 \mu_B$ . However, it can be seen that  $\mu_{eff}$  for  $Mn_{12}$ -stearate at 300 K is about  $12.3 \mu_B$  as shown in Figure 6. The main conclusion that can be deduced from 300 K value is that there are appreciable exchange interactions present and not all of the spin states of the cluster are equally thermally populated.

$Mn_{12}$ -stearate exhibits a hysteresis loop at 2 K, as shown in Figure 7. The measurement was performed after the sample has been cooled to 2 K in zero field. After thermal equilibration, the magnetization was measured as the magnetic field was increased to 25.0 kG, decreased to zero, reversed in direction to -25.0 kG and then returned to zero. A large magnetic anisotropy of  $Mn_{12}$  clusters cause to the hysteresis



**Figure 7.** Magnetic hysteresis loop of  $Mn_{12}$ -stearate at 2 K.

loop for  $Mn_{12}$ -stearate, which involves several steps resulting from the magnetization tunneling. The shape of hysteresis loop was believed to be caused by individual molecule and not by long-range ordering since frozen solutions of  $Mn_{12}$ -Ac and polymer-doped  $Mn_{12}$ -Ac samples also show similar shapes of hysteresis loops with  $Mn_{12}$ -Ac polycrystalline samples. It should be noted that each sample shows different shape of hysteresis curves and its reason is still argued.<sup>8c</sup>  $Mn_{12}$ -stearate in this study shows the similar shape of hysteresis loop with that of  $Mn_{12}$ -methyl-4-benzoate compound.<sup>8e</sup>

## Conclusion

Various chemical analyses showed that some of acetates in  $Mn_{12}$ -Ac compound were successfully substituted with stearate. The magnetic hysteresis loop of  $Mn_{12}$ -stearate shows several steps, which indicates magnetization tunneling of  $Mn_{12}$  cluster complexes. This new compound of  $Mn_{12}$ -stearate is a versatile compound since it is soluble in most organic solvents. This novel property could be applied in materials processing such as spin casting using solution deposition to fabricate nano-sized magnetic quantum dots since  $Mn_{12}$ -stearate contains stabilized  $Mn_{12}$  cluster.

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