

## Solvate Effect on Magnetic Relaxation in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{CH}_2\text{Cl})_{16}(\text{H}_2\text{O})_4]$ Containing Complexes

Chi-Dong Park, Seog Woo Rhee, YooJin Kim, WonSuk Jeon,  
Duk-Young Jung,<sup>\*</sup> Do-hyeon Kim,<sup>†</sup> Youngkyu Do,<sup>‡</sup> and Hyeong-Cheol Ri<sup>‡</sup>

*Department of Chemistry-BK21 and the Institute of Basic Science, SungKyunKwan University, Suwon 440-746, Korea*

*<sup>†</sup>Department of Chemistry, School of Molecular Science-BK21 and Center for Molecular Design and Synthesis,  
Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Korea*

*<sup>‡</sup>National Research Laboratory for the Material Science, Korea Basic Science Research Institute, Daejeon 305-806, Korea*

Received April 24, 2001

**Keywords :** Single-molecule magnets, Manganese, Magnetic relaxation, Solvate effect.

Single-molecule magnets (SMMs) are attracting extensive interests because they are composed with well-defined magnetic molecules of nano-scale size.<sup>1</sup> Several examples of SMM have been reported, which contain manganese ( $\text{Mn}_{12}$  and  $\text{Mn}_4$ ) and iron ( $\text{Fe}_8$  and  $\text{Fe}_4$ ) ions.<sup>1</sup> One of the most extensively studied SMMs is dodecanuclear manganese carboxylate complex,  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{CO}_2\text{H} \cdot 4\text{H}_2\text{O}(\text{Mn}_{12}\text{-Ac})$ ,<sup>2</sup> its derivative compounds,  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4] \cdot \text{solv}$  ( $\text{R}=\text{Et}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{Ph}$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{-2-Br}$ ,  $\text{C}_6\text{H}_4\text{-2-Cl}$  and other complex ligands;  $\text{solv} = \text{solvate molecules}$ )<sup>3</sup> and one-electron (and two-electron) reduced  $\text{Mn}_{12}$  complexes.<sup>4</sup> Some of these  $\text{Mn}_{12}$  compounds show magnetic properties different from that for  $\text{Mn}_{12}\text{-Ac}$  ( $S=10$ ). So far the origin of the different rate of tunneling for the various  $\text{Mn}_{12}$  complexes is unclear whether the different ground states, high order zero-field interaction, or other uncovered reasons present this phenomena as a critical parameter.

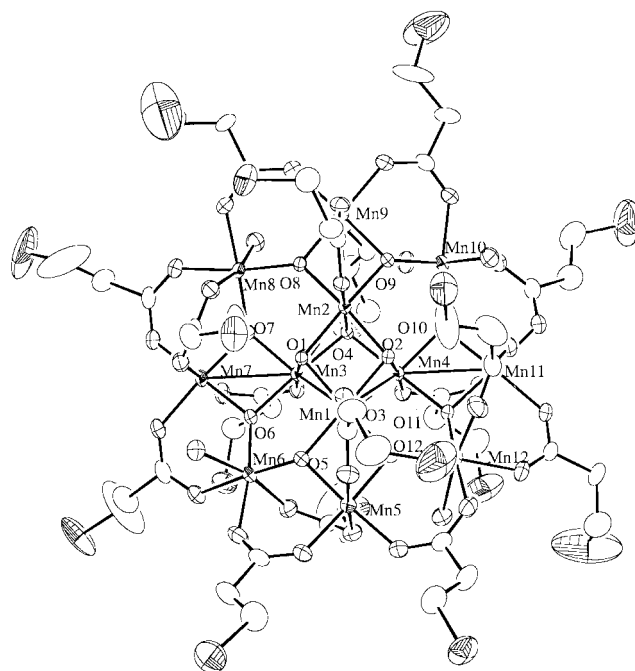
In this paper we describe preparation, crystal structure and magnetic properties of a new SMM with different solvate molecules,  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{CH}_2\text{Cl})_{16}(\text{H}_2\text{O})_4] \cdot \text{solv}$  [ $\text{solv} = 0.5\text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (complex 1) and  $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$  (complex 2)] of which the core molecule is called as  $\text{Mn}_{12}\text{-PrCl}$ . The magnetic relaxation behaviors are presented to demonstrate the correlation of the magnetic properties and solvate molecules locating among the  $\text{Mn}_{12}\text{-PrCl}$  molecules.

$\text{Mn}_{12}\text{-Ac}$  was synthesized according to the reported method.<sup>2a</sup> To a slurry of complex  $\text{Mn}_{12}\text{-Ac}$  (1.0 g, 0.5 mmol) in toluene (25 mL), 3-chloropropionic acid (1.45 g, 13.4 mmol) was added. The reaction mixture was stirred and solvent was evaporated under reduced pressure to remove acetic acid. The ligand exchange reaction using 3-chloropropionic acid was repeated twice. The crystals of complex 1 were grown in  $\text{CH}_2\text{Cl}_2$ /hexane and the crystals of complex 2 were grown in toluene/hexane solution.

Both complex 1 and complex 2 crystallize in the triclinic space group  $P\bar{1}$  and contain discrete  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{CH}_2\text{Cl})_{16}(\text{H}_2\text{O})_4]$  molecules along with different solvated molecules (Figure 1). Overall, the structure of 1 completely superposes on 2 and both complexes present similar but

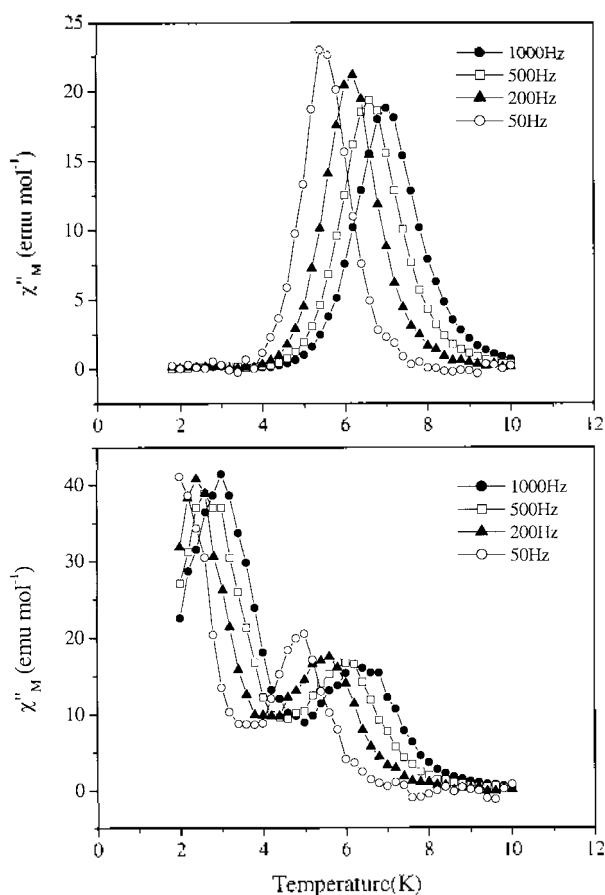
lower symmetric packing compared to that of the  $\text{Mn}_{12}\text{-Ac}$ .<sup>2a</sup> The inner core  $[\text{Mn}(\text{IV})_4\text{O}_4]^{8+}$  cubane unit is held within a non-planar ring of eight  $\text{Mn}(\text{III})$  atoms by eight  $\mu_3$ -oxide atoms. Outer  $\text{Mn}(\text{III})$  ( $3d^4$ ) atoms show a Jahn-Teller (J-T) distortion with an elongation along the axes approximately parallel to the unique molecular  $C_2$  axis. The four water molecules on four  $\text{Mn}(\text{III})$  are all on J-T axial sites, and their bond lengths are similar to the axial  $\text{Mn-O}(\text{carboxylato})$  values. It should be noted that the complexes 1 and 2 have the binding sites of water and carboxylate group same as those of the  $\text{Mn}_{12}\text{-Ac}$ , which is comparable to  $\text{Mn}_{12}\text{-propionate}$  and  $\text{Mn}_{12}\text{-O}_2\text{CC}_6\text{H}_4\text{-4-Me}$  compounds with isomeric form of water and carboxylates coordinating  $\text{Mn}(\text{III})$ .<sup>3b</sup>

Out-of-phase ac magnetic susceptibility ( $\chi_M''$ ) data are



**Figure 1.** Molecular structure of  $\text{Mn}_{12}\text{-PrCl}$  complex 1 (solvated by  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$ ). Ellipsoids are drawn for 50% probability, and hydrogen atoms have been omitted for clarity. The structure of  $\text{Mn}_{12}\text{-PrCl}$  complex 2 (solvated by  $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$ ) is fully superposed over complex 1.

<sup>\*</sup>Corresponding Author. e-mail: dyjung@chem.skku.ac.kr; Tel: +82-31-290-7074; Fax: +82-31-290-7075



**Figure 2.** Plots of the out-of-phase ac magnetic susceptibility  $\chi_M''$  vs. temperature for polycrystalline samples of the  $Mn_{12}$ -PrCl complex **1** (upper) and **2** (lower). Data were collected under zero magnetic field at the frequencies of (○) 50, (▲) 200, (□) 500 and (●) 1000 Hz.

measured for both **1** and **2** complexes in the region 1.9 to 10 K. at different frequencies in zero field (Figure 2). Both complexes exhibit frequency-dependent ac  $\chi_M''$  peaks, demonstrating both complexes behave as SMMs. Complex **2** has a predominant peak in the region 2 to 4 K as well as minor peak at around 5 to 7 K, however complex **1** has a large single peak in the region 4 to 7 K and other peak is not observed at lower temperature. The principal differences between two complexes in the solid state are solvate molecules and the resulting unit cell volumes. The present  $Mn_{12}$ -PrCl solv compounds demonstrate similar variation with  $[Mn_{12}O_{12}(O_2CC_6H_4-4-Me)_{16}(H_2O)_4] \cdot solv$  (solv =  $3H_2O$  or  $HO_2CC_6H_4-4-Me$ ) complexes.<sup>3b</sup> The latter compounds reported have not only different solvates but also isomeric forms resulting from different coordinated water arrangement, thus the origin of different relaxation behaviors could not be concluded since two different effects coexist at the same time. On the contrary, in the present  $Mn_{12}$ -PrCl case, it is suggested that the magnetic relaxation is strongly correlated with solvate molecules since complexes **1** and **2** possess the same configuration of waters and carboxylates bound to Mn(III) ions.

Other physical measurements such as high-field EPR experiments are needed to determine whether complexes **1** and **2** differ in their ground-state spins. Understanding their magnetic relaxation data should give insight into the mechanism of the magnetization tunneling. In addition, the space packing of  $Mn_{12}$  cluster molecules in solid state may be strongly correlated with solvate molecules, which could be controlled by synthetic procedure utilized in the crystal growing steps. The potential application of SMMs in the solid state device needs the information of solvate effect influencing upon magnetic property of each compound.

**Acknowledgment.** This work was supported by the Electron Spin Science Center at POSTECH, which was established by the KOSEF. The KBSRI provided us with SQUID magnetometer measurements.

**Supplementary Materials:** Crystallographic data for **1** and **2** are available from the corresponding author upon request.

+ *Crystal data.* Complex **1**:  $C_{48.5}H_{77}Cl_{17}Mn_{12}O_{50}$  [ $Mn_{12}O_{12}(O_2CCH_2CH_2Cl)_{16}(H_2O)_4$ ]  $\cdot 0.5CH_2Cl_2 \cdot 2H_2O$ ,  $M_r=2722.07$ , triclinic  $P\bar{1}$ ,  $a=16.000(1)$  Å,  $b=18.040(1)$  Å,  $c=18.073(1)$  Å,  $\alpha=91.549(1)^\circ$ ,  $\beta=94.343(1)^\circ$ ,  $\gamma=109.936(1)^\circ$ ,  $V=4881.9(5)$  Å<sup>3</sup>,  $Z=2$ ,  $T=293$  K,  $\mu=2.026$  mm<sup>-1</sup>,  $D_c=1.802$  Mg m<sup>-3</sup>,  $R_1=0.0752$  (22454 unique reflections). Anal. Calcd: C, 21.40; H, 2.85 Found: C, 21.78; H, 2.88.

Complex **2**:  $C_{51}H_{77}Cl_{17}Mn_{12}O_{50}$  [ $Mn_{12}O_{12}(O_2CCH_2CH_2Cl)_{16}(H_2O)_4$ ]  $\cdot CH_2ClCH_2CO_2H$ ,  $M_r=2752.10$ , triclinic  $P\bar{1}$ ,  $a=16.355(2)$  Å,  $b=17.635(3)$  Å,  $c=19.243(3)$  Å,  $\alpha=88.682(3)^\circ$ ,  $\beta=82.193(3)^\circ$ ,  $\gamma=68.800(2)^\circ$ ,  $V=5125(1)$  Å<sup>3</sup>,  $Z=2$ ,  $T=293$  K,  $\mu=1.951$  mm<sup>-1</sup>,  $D_c=1.754$  Mg m<sup>-3</sup>,  $R_1=0.0954$  (23418 unique reflections). Anal. Calcd: C, 22.26; H, 2.82 Found: C, 24.11; H, 2.99.

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