High Spin Molecules: $[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ and the One-electron Reduction Product $[PPh_4][Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$

Hui-Lien Tsai,* Tyn-Yih Jwo, Gene-Hsiang Lee,† and Yu Wang†
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, R.O.C.
†*Instrumentation Center, College of Science, National Taiwan University, Taipei, Taiwan 10601, R.O.C.*

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The complex of $[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]$ was reduced by PPh_4I to give a reduced complex $[PPh_4][Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$. Crystal structures of both complexes were determined by the X-ray method. The dc magnetic susceptibility measurements indicate that the neutral and reduced complexes are high spin species.

Single-molecule magnets (SMM) are attracting extensive attention because they represent nanoscale magnetic particles of a well-defined size.[1-6] They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (AC) magnetic susceptibility. The remarkable magnetic properties of a SMM arise from the SMM's high-spin ground state (S) split by a large negative axial zero-field splitting (D) which results in an anisotropy energy barrier of $KV = |D|\hat{S}^2$.[7] The first SMM reported was $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2HOAc\cdot 4H_2O$ (**1**) with S = 10 ground state and a negative zero-field splitting of -0.5 cm^{-1}.[1,2,5] The one electron reduction complex $[PPh_4][Mn_{12}O_{12}(O_2CC_2H_5)_{16}(H_2O)_4]$ (**2**) was also reported to have S = 19/2 ground state and behave as a SMM.[2,6] We herein describe the preparation and X-ray structures of two new SMMs, $[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_4]\cdot 3CH_2Cl_2\cdot 2H_2O$ (**3**) and its reduced $[PPh_4][Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]\cdot 2CH_2Cl_2\cdot 2H_2O$ (**4**) that differ in their space group and the positioning of their H_2O ligands on the Mn_{12} complexes.

The acetate derivative, complex **3** may be synthesized through the removal of CH_3CO_2H as toluene azoetrope from the reaction of complex **1** with excess ClH_2CCOOH. The neutral complex **3** shows a chemically reversible reduction at 0.53 V vs ferrocene/ferrocenium. Reduction of **3** with PPh_4I yields the stable complex **4**. Both **3** and **4** have been recrystallized from a mixture of dichloromethane and hexane, and afforded suitable crystals for the X-ray crystal structure analysis.

X-Ray data were measured on an Enraf-Nonius CAD4 and a Bruker-axs, SMART CCD diffractometer with graphite monochromatized Mo-Kα radiation for complexes **3** and **4**, respectively.[8]

The ORTEP plot of the complex **3** is shown in Figure 1(a). The structure of complex **3** is quite similar in many respects to complex **1**.[9] Complex **3** possesses a $[Mn_{12}(\mu_3\text{-}O)_{12}]$ core comprising a central $[Mn^{IV}{}_4O_4]^{8+}$ cubane held within a nonplanar ring of eight Mn^{III} ions by eight μ_3-O^{2-} ions. Peripheral ligation of complex **3** is proved by sixteen μ_2-carboxylate groups and four H_2O ligands. The Mn-O bond distances make it clear that all of the atoms in the central cubane are Mn^{IV} ions, while the ring consists of eight Mn^{III} ions. These assignments supported by the marked Jahn-Teller elongation of the axial Mn-O bonds (2.093-2.260 Å), which are on average 0.255 Å longer than the analogous equatorial Mn-O bonds (1.873-2.012 Å). Complex **3** has one H_2O ligand on each of four Mn^{III} ions; Mn(4), Mn(6), Mn(4A), and Mn(6A) which are bonded to two Mn^{IV} ions via two μ_3-O^{2-} ions.

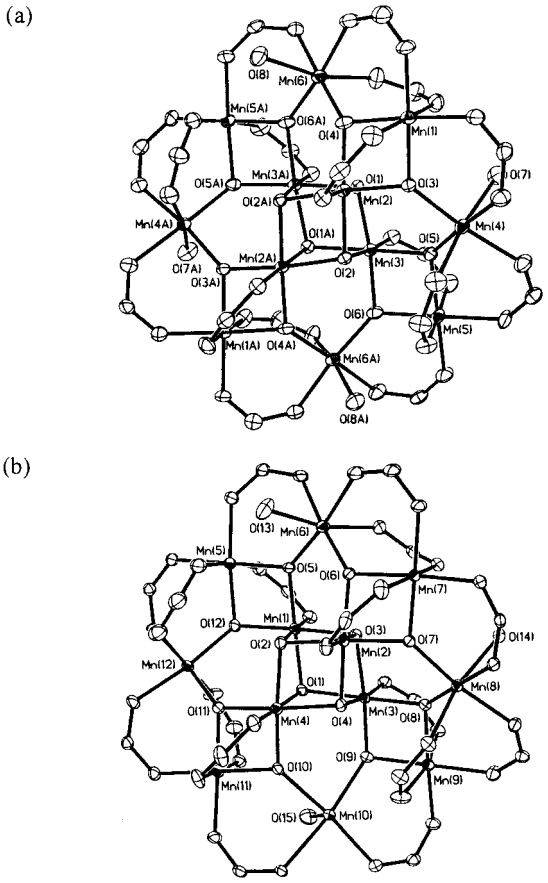

Figure 1. (a) Molecular structure of complex **3** and (b) molecular structure of the anion of complex **4**. The ClH_2C-groups of the acetate ligands, PPh_4 ion, the H_2O and CH_2Cl_2 solvate molecules are omitted for clarity.

An ORTEP plot of the anion of **4** is shown in Figure 1(b). The structure shows that the single added electron produces a valence trapped $Mn^{II}Mn^{III}{}_7Mn^{IV}{}_4$ anion rather than a $Mn^{III}{}_9Mn^{IV}{}_3$ ion. Compared to complex **2**,[2] complex **4** has one interesting feature. Unlike complex **2**, complex **4** has only three bound H_2O ligands, Mn(10) being five coordinate with one H_2O ligand. The other two H_2O ligands are bonded to Mn(6) and Mn(8), which is bonded to two Mn^{IV} ions via two μ_3-O^{2-} ions. For Mn(10) atom, the equatorial Mn-O bond lengths show a pronounced elongation (2.070-2.188 Å) relative

to the corresponding bond distances (1.860-1.989 Å) for the Mn^{III} ions. Clearly, the Mn(10) atom in complex **4** is a Mn^{II} ion, and it does not exhibit a Jahn-Teller distortion as seen for all the Mn^{III} ions in the complex **3**.

Variable-temperature dc magnetic susceptibility data were collected for polycrystalline samples of complexes **3** and **4** in an applied filed of 1.0 kG, and in the temperature range 2.00–310.0 K, which were measured by a SQUID magnetometer (Quantum Design, MPMS-7).[10] The samples were embedded in eicosane wax to prevent any torquing of the polycrystalline in the magnetic field. Pascal's constants[11] were used to estimate the diamagnetic corrections and to give the values of -1.06×10^{-3} and -1.21×10^{-3} emu/mol for complexes **3** and **4**, respectively. As can be seen in Figure 2, for complex **3** μ_{eff} per molecule slowly decreases from 12.96 μ_B at 310.2 K to 12.20 μ_B at 170.2 K, and then increases, reaching a maximum of 18.43 μ_B at 14.0 K, finally decreases to 8.19 μ_B at 2.00 K. The data for the one-electron reduced complex **4** show similar temperature dependence; μ_{eff} per molecule slowly decreases from 12.39 μ_B at 310.8 K to 11.55 μ_B at 170.0 K, and then increases, reaching a maximum of 20.32 μ_B at 11.99 K, finally decreases to 7.56 μ_B at 2.00 K. This behavior is similar to that observed for complex **1**; which has a μ_{eff} values of 12.17 μ_B at 300.0 K, with decreasing temperature increases to a maximum of 20.79 μ_B at 15.0 K, whereupon there is a decrease to 15.79 μ_B at 5.00 K.[2]

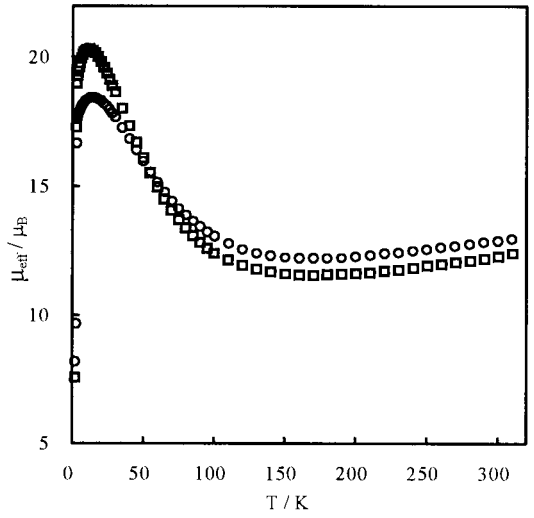

Figure 2. Plots of μ_{eff} versus temperature for polycrystalline samples of complex **3** (○) and complex **4** (□).

If there were no magnetic exchange interaction present in a $Mn^{III}{}_8Mn^{IV}{}_4$ and $Mn^{II}Mn^{III}{}_7Mn^{IV}{}_4$ complexes, then the spin-only effective magnetic moment with g = 2.0 should be μ_{eff} = 15.87 μ_B and μ_{eff} = 16.22 μ_B for complexes **3** and **4**, respectively. It is clear from the values of μ_{eff} per molecule for complexes **3** and **4** at 310.0 K that there are in both complexes appreciable exchange interactions present. The exchange interactions in the $Mn^{II}Mn^{III}{}_7Mn^{IV}{}_4$ complex **4** are greater than those in complex **3**, for the μ_{eff} per molecule for complex **4** at 310.0 K is much lower than its expected spin–only value compared to the $Mn^{III}{}_8Mn^{IV}{}_4$ complex **3**. The increase in μ_{eff} with decreasing temperature to a maximum at low temperatures is expected the fact that as the temperature is decreased only one high-spin state is thermally populated. This $Mn^{III}{}_8Mn^{IV}{}_4$ complex **1** has been established to have an S = 10 ground state. Complexes **3** and **4** must have a ground state with a relatively large spin.

Reduced magnetizations and AC magnetic measurements are in progress to determine which total spin complexes **3** and **4** differ in their ground state. From primary results, they show frequency dependence in the out-of-phase AC magnetic susceptibilities and prove to be SMMs.[12] Furthermore, Mn_{12} SMMs also exhibit steps on hysteresis loops, which are characteristic behaviors of magnetic quantum tunneling.[1,13] The hysteresis loops measurements on complexes **3** and **4** will give insight into the mechanism of magnetization tunneling.

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References and Notes

1 R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature*, **365**, 141 (1993); L. Thomas, F. Lionti, R. Ballou, D Gatteschi, R. Sessoli, and B. Barbara, *Nature*, **383**, 145 (1996).

2 R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **115**, 1804 (1993); A. R. Schake, H.-L. Tsai, R. J. Webb, K. Folting, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **33**, 6020 (1994); H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **117**, 301 (1995).

3 S. M. J. Aubin, N. R. Dilley, M. Wemple, M. B. Maple, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc*., **120**, 839 (1998).

4 G. Aromi, S. M. J. Aubin, M. A. Bolcar, G. Christou, H. J. Eppley, K. Folting, D. N. Hendrickson, J. C. Huffman, R. C. Squire, H.-L. Tsai, S. Wang, and M. Wemple, *Polyhedron*, **17**, 3005 (1998).

5 S. M. J . Aubin, Z. Sun, I. A. Guzei, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Chem. Commun*., **1997**, 2339; D. Ruiz, Z. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl*., **37**, 300 (1998); Z. Sun, D. Ruiz, E. Rumberger, C. D. Incarvito, K. Folting, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **37**, 4758 (1998); Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou, and D. N. Hendrickson, *Chem. Commun*., **1999**, 1973.

6 S. M. J. Aubin, S. Spagna, H. J. Eppley, R. E. Sager, G. Christou, and D. N. Hendrickson, *Chem. Commun.*, **1998**, 803; S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A. L. Rheingold, G. Christou, and D. N. Hendrickson *Inorg. Chem.*, **38**, 5329 (1999).

7 D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, *Science*, **265**, 1054 (1994); J. Villain, F. Hartman-Boutron, R. Sessoli, and A. Rettori, *Europhys. Lett.*, **27**, 159 (1994).

8 Crystal data of complex $\mathbf{3}\cdot 3CH_2Cl_2\cdot 2H_2O$: $C_{35}H_{50}Cl_{22}Mn_{12}O_{50}$, *FW* = 2709.93, monoclinic, space group *C2/c*, *a* = 25.238(2), *b* = 13.226(2), *c* = 26.199(5) Å, β = 94.761(13)°, *V* = 8715(2) Å^3, *Z* = 4, D_{cal} = 2.065 g/cm^3, $R(R_w)$ = 0.0910(0.2776) (7645 unique reflections with I> 2σ(I)). Crystal data of complex $\mathbf{4}\cdot 2CH_2Cl_2\cdot 2H_2O$: $C_{58}H_{66}Cl_{20}Mn_{12}O_{49}P$, *FW* = 2946.36, orthorhombic, space group *Fdd2*, *a* = 51.3413(7), *b* = 61.6796(7), *c* = 12.8787(1) Å, *V* = 40783.1(8) Å^3, *Z* = 16, D_{cal} = 1.919 g/cm^3, $R(R_w)$ = 0.0490 (0.1204) (22937 unique reflections with I> 2σ(I)).

9 T. Lis, *Acta Cryst.*, **B36**, 2042 (1980).

10 Satisfactory elemental analysis data (C, H, Mn) were obtained. Anal. $\mathbf{3}\cdot 7H_2O$; Found: C, 15.58; H, 2.08; Mn, 25.24%. Calcd. for $C_{32}H_{54}Cl_{16}Mn_{12}O_{55}$: C, 15.21; H, 2.14; Mn, 25.90%. Anal. $\mathbf{4}\cdot 3H_2O$; Found: C, 24.11; H, 2.32; Mn, 23.10%. Calcd. for $C_{56}H_{64}Cl_{16}Mn_{12}O_{50}P$: C, 24.07; H, 2.31; Mn, 23.59%.

11 "Theory and Application of Molecular Paramagnetism," ed. by E. A. Boudreaux, and L. N. Mulay, J. Wiley & Sons, New York (1976).

12 H.-L. Tsai, T.-Y. Jwo, C.-S. Wur, G.-H. Lee, and Y. Wang, unpublished results.

13 J. R. Friedman, M. P. Sarachik, J. Tejada, J. Maciejewski, and R. Ziolo, *J. Appl. Phys.*, **79**, 6031 (1996); J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.*, **76**, 3830 (1996).