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Antiferromagnetic Fe^{III}_6 Ring and Single-Molecule Magnet $Mn^{II}_3Mn^{III}_4$ Wheel

Satoshi Koizumi,[†] Masayuki Nihei,[†] Motohiro Nakano,[‡] and Hiroki Oshio*,[†]

Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan, and
Department of Molecular Chemistry, Graduate School of Engineering, Osaka University,
Toyonaka, Osaka 560-0043, Japan

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Reactions of a quadridentate ligand [*N*-(2-hydroxy-5-nitrobenzyl)-iminodiethanol] with iron and manganese chloride in methanol yielded an antiferromagnetic Fe^{III}_6 ring and a single-molecule magnet $Mn^{II}_3Mn^{III}_4$ wheel, respectively.

Single-domain magnets contain high-spin molecules with Ising magnetoanisotropy, which are classified as single-molecule magnets (SMMs).[1] Since the discovery of a manganese oxo cluster $[Mn_{12}]$,[2] several types of SMMs have been reported with recent focus being on larger SMMs in which new properties might appear in the border between mesoscopic and bulk properties.[3] Quantum tunneling of the magnetization (QTM)[4] and quantum phase interference,[5] which are important in the preparation of quantum devices,[6] are two phenomena exhibited by SMMs. QTM occurs between two spin sublevels separated by the tunnel splitting energy ($\Delta E_{\mathrm{tunnel}}$), and its transition probability increases as the value of $\Delta E_{\mathrm{tunnel}}$ becomes large.[7] $[Mn_{12}]$ and $[Fe_8]$[8] have been shown to have relatively small values of $\Delta E_{\mathrm{tunnel}}$.[5,9] However, complexes with antiferromagnetic ring systems are expected to have larger $\Delta E_{\mathrm{tunnel}}$ values and might exhibit coherent tunneling of the Néel vector.[10] Metal cyclic compounds with different sizes have been reported recently.[3a,11] Molecular wheels of $[Mn_7(OMe)_{12}(dbm)_6]$ (dbm = dibenzoylmethane)[3e] and $[Fe_7(OMe)_6(HL_6)]Cl_3$ [H_2L = 2-(3-methoxysalicylideneamino)ethanol][11f] have high-spin ground states of $S = {}^{17}/_{2}$ and ${}^{27}/_{2}$, respectively, but their superparamagnetism was not proven. Large wheels of $[Mn_{84}O_{72}(O_2CMe)_{78}$-$(OMe)_{24}(MeOH)_{12}(H_2O)_{42}$-$(OH)_6]$[3a] ($S = 6$) and $[Ni_{12}(chp)_{12}$-$(O_2CMe)_{12}(H_2O)_6(thf)_6]$ ($S = 12$ and chp = 6-chloro-2-pyridonate)[3d] were found to be SMMs. The number of wheel SMMs was, however, limited, and more examples are required to understand and exploit the quantum phenomena characteristic of cyclic compounds. We report here an antiferromagnetic Fe^{III}_6 ring ($S = 0$) and a mixed-valence $Mn^{II}_3Mn^{III}_4$ wheel ($S = {}^{21}/_{2}$) that is an SMM.

Reactions of quadridentate ligands [H_3L = *N*-(2-hydroxy-5-nitrobenzyl)iminodiethanol][12] with $FeCl_3$ and $MnCl_2{\cdot}4H_2O$ in methanol, followed by recrystallization from DMSO/diethyl ether and 1,2-dichloroethane, yielded the molecular ring complex $[Fe^{III}_6L_6]{\cdot}H_2O$ ($\mathbf{1}{\cdot}H_2O$) and the molecular wheel

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* To whom correspondence should be addressed. E-mail: oshio@chem.tsukuba.ac.jp.

[†] University of Tsukuba.

[‡] Osaka University.

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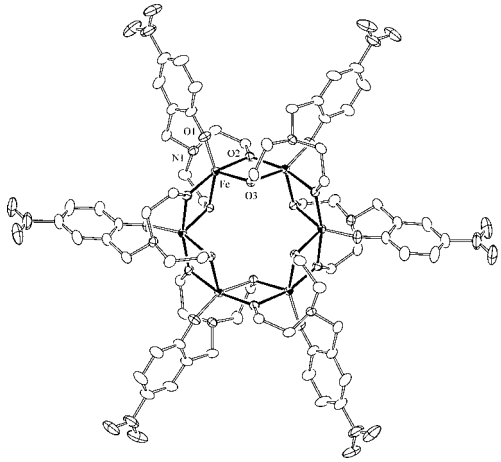

Figure 1. ORTEP diagram of **1** with 30% probability.

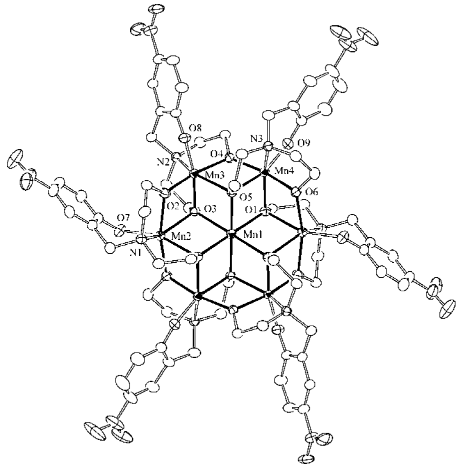

Figure 2. ORTEP diagram of **2** with 30% probability.

$[Mn^{II}_3Mn^{III}_4L_6]\cdot 7C_2H_4Cl_2$ ($\mathbf{2}\cdot 7C_2H_4Cl_2$), respectively.[13] $\mathbf{1}\cdot H_2O$ crystallizes in the trigonal space group $R\bar{3}$with the complex molecule situated on a $\bar{3}$ inversion axis. In the complex molecule, six Fe^{III} ions are arranged in a planar cyclic structure (Figure 1) in which Fe^{III} ions are doubly bridged by two alkoxo groups in a μ_2 fashion with bridging Fe−O−Fe angles of 105.3(2)° and 104.9(2)°. The coordination sites of each Fe^{III} ion are occupied by one nitrogen and three oxygen atoms from a single L^{3-} and two oxygen atoms from a neighboring unit in the ring. Coordination bond lengths with oxygen atoms are in the range of 1.930(4)−2.014(3) Å and are shorter than that involving the nitrogen atom [2.220(4) Å].

$\mathbf{2}\cdot 7C_2H_4Cl_2$ crystallizes in the monoclinic space group $P2_1/n$, and the complex molecule lies on a crystallographic center of symmetry (Figure 2). Seven manganese ions linked by six trianionic ligands compose the wheel structure. Because complex **2** is neutral, the molecule is a mixed-valence cluster with three Mn^{II} and four Mn^{III} ions. On the bases of bond valence sum calculations[14] and the presence of Jahn−Teller distortion in Mn^{III} ions, the two manganese ions on the rim (Mn2) and the one in the center (Mn1) are Mn^{II} ions, and the other four manganese ions (Mn3 and Mn4) are Mn^{III} ions. In the wheel, six μ_2-alkoxo groups (O2, O4, and O6) bridge the manganese ions on the rim, which themselves are linked to the central ion through six μ_3-groups (O1, O3, and O5) acting as spokes to form the wheel structure. The coordination geometry of the Mn^{II} ions (Mn1 and Mn2) can be described as quasioctahedral, and they have O_6 and N_1O_5 chromophores with bond lengths of 2.194(5)−2.211(5) and 2.048(5)−2.259(5) Å, respectively. The Mn^{III} ions (Mn3 and Mn4) have axially elongated coordination geometry with the Jahn−Teller elongation axes along N2−Mn3−O5 and N3−Mn4−O1, Mn4−O1, respectively. Coordination bond lengths with axial atoms are 2.115(5)−2.239(6) Å, and the bond lengths involving the equatorial atoms are in the range of 1.859(5)−2.097(5) Å.

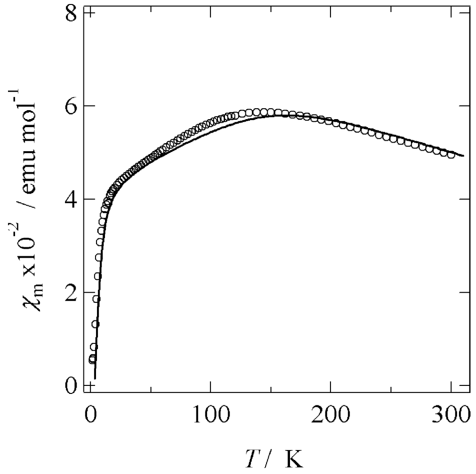

Figure 3. χ_m versus T plot for $\mathbf{1}\cdot H_2O$. The solid line results from the theoretical calculation using the value in the text.

A powdered sample of $\mathbf{1}\cdot H_2O$ showed antiferromagnetic behavior in the temperature range of 1.8−300 K (Figure 3). The molar magnetic susceptibility for $\mathbf{1}\cdot H_2O$ increased as the temperature was lowered, reaching a maximum at 120 K, and decreased rapidly at 20 K. The temperature dependence of the magnetic data was very similar to those for the reported six-membered Fe^{III} rings,[15] confirming that the molecule has an $S = 0$ spin ground state. The exchange coupling constant (J) between Fe^{III} ions was estimated to be $-8.1(1)$ cm^{-1} with a g_{Fe} value of 2.02(2).[16]

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(13) Anal. Calcd (found) for dried **1**: C, 42.75 (42.56); H, 4.24 (4.32); N, 9.06 (9.18). (b) Crystal data for $\mathbf{1}\cdot H_2O$ ($C_{66}H_{80}Fe_6N_{12}O_{31}$): orange block (0.2 × 0.2 × 0.3 mm^3), $M = 1872.51$, trigonal $R3$ with $a = 30.208(7)$ Å, $c = 8.454$ (3) Å, $V = 6681(3)$ Å^3, $Z = 3$, $d_{calc} = 1.396$ g cm^{-3}, $T = -70$°C. Final R1 = 0.0618 and wR2 = 0.1929. (c) Anal. Calcd (found) for dried **2**: C, 41.64 (41.80); H, 4.13 (4.56); N, 8.83 (8.57). (d) Crystal data for $\mathbf{2}\cdot 7C_2H_4Cl_2$ ($C_{80}H_{106}Cl_{14}Mn_7N_{12}O_{30}$): dark red block (0.2 × 0.3 × 0.3 mm^3), $M = 2596.69$, monoclinic $P2_1/n$ with $a = 17.240(4)$ Å, $b = 11.720(3)$ Å, $c = 27.789(7)$ Å, $\beta = 101.434(5)$°, $V = 5503(2)$ Å^3, $Z = 2$, $d_{calc} = 1.567$ g cm^{-3}, $T = -70$°C. Final R1 = 0.0679 and wR2 = 0.1922.

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(16) The spin Hamiltonian for a six-membered ring can be expressed as $H = J(-S_{ring}^2 + S_{even}^2 + S_{odd}^2) + 2J(S_1\cdot S_4 + S_2\cdot S_5 + S_3\cdot S_6)$, where $S_{odd} = S_1 + S_3 + S_5$, $S_{even} = S_2 + S_4 + S_6$, and $S_{ring} = S_{odd} + S_{even}$. J represents the exchange coupling constant between iron(III) centers. The expression for χ_m was derived by using a Kambe's model with a perturbative correction (Asano, K.; Inoue, K.; Nakano, M.; Miyazaki, Y.; Sorai, M.; Nakatani, K.; Kahn, O. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1749).

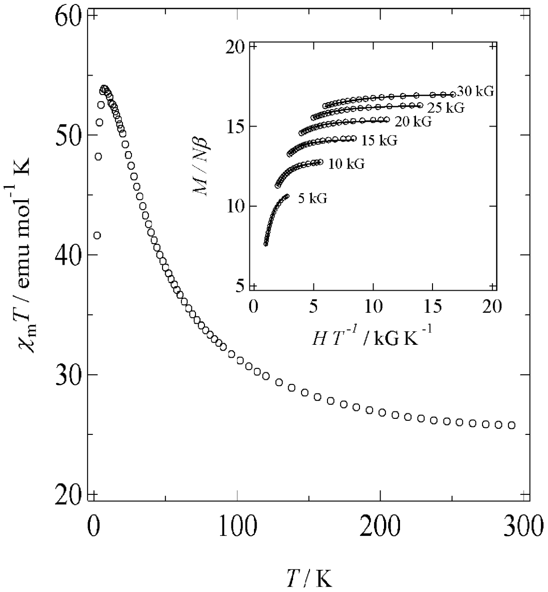

Figure 4. $\chi_m T$ versus T plot and field dependence of magnetization at the indicated magnetic field (inset) for **2**·$7C_2H_4Cl_2$. The solid line shows the best fit using $S = ^{21}/_2$, $g = 1.86$, and $D = -0.2$ cm^{-1}.

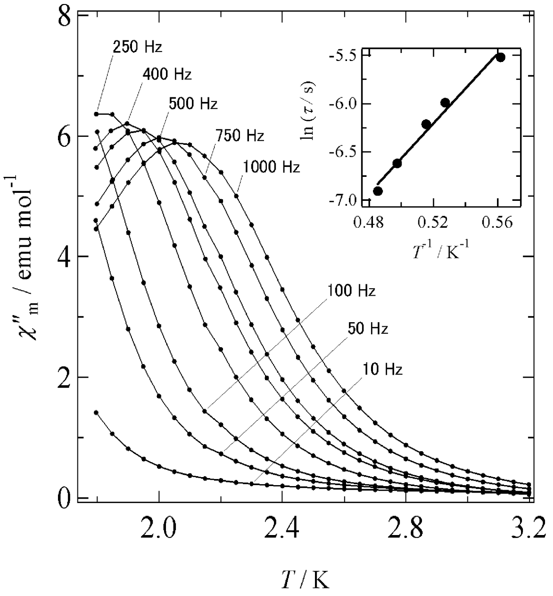

Figure 5. Plots of out-of-phase (χ_m'') ac susceptibility versus T in a 3.0 G ac field oscillating at the indicated frequencies and plot of the ln(τ) vs inverse temperature (T^{-1}) (inset) for **2**·$7C_2H_4Cl_2$.

The temperature dependence of the magnetic susceptibilities for **2**·$7C_2H_4Cl_2$ is shown in Figure 4. The $\chi_m T$ value of 25.71 emu mol^{-1} K at 300 K increased as the temperature was lowered, reaching a maximum value of 53.9 emu mol^{-1} K at 7.0 K. The Curie constant for uncorrelated three Mn^{II} and four Mn^{III} ions is 25.125 emu mol^{-1} K with $g = 2.0$. The sudden decrease in the $\chi_m T$ value below 7.0 K is due to magnetic anisotropy and/or through-space antiferromagnetic interactions. The spin ground state of **2** can be in the range of $S = ^{31}/_2 - ^{1}/_2$. The maximum $\chi_m T$ value at 7.0 K suggests that **2** has relatively large spin ground states such as $S = ^{21}/_2$ and $^{19}/_2$.[17] Supposing a ferrimagnetic situation with an antiparallel spin on the central Mn1 ion (spin down) to the spins on the Mn2 − Mn4 ions (spin up) on the rim, the spin ground state would be $S = ^{21}/_2$. Schiff bases with an alkyl alcohol group bridge metal ions, and alkoxides sometimes propagate ferromagnetic interactions.[11f] It should be noted, however, that magnetic interactions between metal ions are very sensitive to bridging bond angles and electronic configuration (number of d electrons). The ferromagnetic pathways in **2** were attained by the accidental orthogonality of magnetic orbitals, whereas this was broken in **1**, leading to the $S = 0$ spin ground state.

Magnetization data collected in the ranges 1.8−5.0 K and 5−30 kG for **2** were fitted including the isotropic Zeeman and axial ZFS terms (Figure 4 inset). Assuming that only the ground state is populated, the best fit was obtained with $g = 1.86$, $D = -0.2$ cm^{-1}, and $S = ^{21}/_2$ (Figure 4 inset). The fit for $S = ^{19}/_2$ was inferior, and thus we conclude that **2** has an $S = ^{21}/_2$ spin ground state.

ac magnetic susceptibility measurements for polycrystalline samples of **2**·$7C_2H_4Cl_2$ were performed in the temperature range from 1.8 to 4.0 K with a 3.0 G ac field oscillating at 10−1000 Hz. **2**·$7C_2H_4Cl_2$ gave frequency-dependent in-phase (χ_m') and out-of-phase (χ_m'') signals, of which the peak maxima shifted to a lower temperature as the ac frequency decreased (Figures 1S, Supporting Information, and 5). The ac susceptibility data show that **2**·$7C_2H_4Cl_2$ is an SMM. The derived effective energy barrier to magnetization reversal (ΔE) was estimated to be 18.1 K with a preexponential factor of $\tau_0 = 1.63 \times 10^{-7}$ s. In summary, a mixed-valence Mn^{II,III} SMM wheel and an antiferromagnetic Fe^{III} ring were prepared by using the same ligand and different metal sources. Low-temperature magnetic measurements to observe quantum behaviors are currently underway.

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Supporting Information Available: Crystallographic details (CIF) for **1**·H_2O and **2**·$7C_2H_4Cl_2$. Plots of in-phase signal (χ_m') versus T for **2**·$7C_2H_4Cl_2$ (Figure 1S). This material is available free of charge via the Internet at http://pub.acs.org.

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[17] Curie constants for $S = ^{21}/_2$ and $^{19}/_2$ states are 60.375 and 49.875 emu mol-1 K, respectively, with $g = 2.0$.