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Raising the Spin of Fe^{III}_7 Disklike Clusters: The Power of Molecular Spin Frustration

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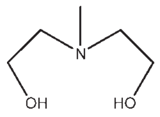
Supporting Information

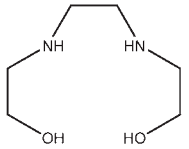
ABSTRACT: Two clusters with a new type of Fe^{III}_7 disklike structure have been prepared; in contrast to other Fe^{III}_7 disks, they possess high ground-state spins ($S = {}^{15}/_2$ and ${}^{21}/_2$), which have been rationalized by analysis of the spin-frustration patterns.

Molecules possessing large numbers of unpaired electrons (i.e., large ground-state spin, S) represent a fascinating subarea of metal cluster chemistry of importance to many fields.[1,2] For example, when coupled with significant easy-axis magnetoanisotropy, such molecules function as single-molecule magnets (SMMs), providing a molecular approach to nanoscale magnetism.[3,4] In contrast, when they possess little or no anisotropy, they are of interest as components for molecule-based magnetic refrigeration based on the magnetocaloric effect.[5] Also, of course, there is the fundamental desire to understand how the signs and relative magnitudes of the many exchange interactions within a cluster yield its high S value.

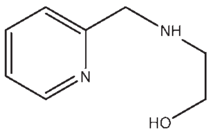
We recently studied the origin of the $S = 11$ ground state of Mn_7 ($4Mn^{II}$, $3Mn^{III}$) complexes with a disklike structure[6,7] and showed it to be due to spin-frustration effects from competing exchange interactions of both ferromagnetic (F) and antiferromagnetic (AF) nature. The relative magnitude of the various exchange parameters (J) suggested that complexes with the maximum $S = 16$ might be attainable, and they were successfully prepared from ligand-induced structural perturbations that altered the relative magnitude of the competing interactions. We then wondered whether spin modification might also be possible in the Fe^{III}_7 disklike complexes that we and others had studied,[8−10] such as $[Fe_7O_3(O_2CR)_9(mda)_3(H_2O)_3]$ (**1**; $mdaH_2$ = *N*-methyldiethanolamine), which possesses a buckled Fe_6 loop around a central Fe atom and an $S = {}^5/_2$ ground state.



$mdaH_2$



$heenH_2$



paeoH

As in our Mn_7 work, the first priority was to identify the origin of the $S = {}^5/_2$ ground state of **1** because we expected all interactions now to be AF. We did this by determining the J values using a published magnetostructural correlation originally developed for dimers that employs both the Fe−O distances and Fe−O−Fe angles.[11] The J values (Figure 1) are indeed all AF but are of two types: relatively strong (-20 to -39 cm^{-1}) and weak (-8.89 cm^{-1}). The ground state can thus be rationalized (Figure 1) as comprising an antiparallel alignment of spins controlled by strong interactions and a parallel alignment of spins controlled by weak ones (Fe1Fe2 and its symmetry partners); i.e., these AF interactions are completely frustrated. This does not offer hope for experimentally changing the $S = {}^5/_2$ ground state of **1** via small ligand-induced perturbations, in contrast to Mn_7.[6,7] With strong AF interactions both between Fe atoms of the outer ring (J_{oo}) and between them and the inner Fe (J_{io}), where o = outer and i = inner, it would clearly take a major modification to affect the ground state, and it is not obvious how to target this. However, this was achieved through happenstance when we recently made a new type of Fe_7 disk while exploring Fe^{III} chemistry with *N,N′*-bis(2-hydroxyethyl)ethylenediamine ($heenH_2$) and 2-(2-pyridylmethyl)aminoethanol (paeoH). This gives much higher ground-state spins.

We have previously used $heenH_2$ in Fe chemistry but not paeoH.[12] In the present work, the reaction of $FeCl_2$ and $heenH_2$ (1:1) in refluxing MeOH gave upon cooling $[Fe_7O_3(OMe)_3(heen)_3Cl_{4.5}(MeOH)(H_2O)_{1.5}]Cl_{1.25}[FeCl_4]_{1/4}$ (**2**), isolated as orange needles of $\mathbf{2}\cdot 2MeOH\cdot {}^1/_2H_2O$ in 10% nonoptimized yield after 7 days. Similarly, the reaction of $Fe(ClO_4)_3$, paeoH, and NEt_3 (1:3:1) in MeOH gave $[Fe_7O_3(OH)_3Cl(paeo)_6](Cl)(ClO_4)_4$ (**3**) as orange crystals of $\mathbf{3}\cdot 2Me_2CO\cdot {}^1/_2Et_2O$ in 14% nonoptimized yield. The cations of **2** and **3** have almost identical Fe_7 cores (Figure 2)[13] consisting of a near-planar Fe^{III}_6 hexagon linked to a central Fe^{III} ion by three μ_3-O^{2-} ions and lying 1.437 Å (**2**) or 1.484 Å (**3**) above the Fe_6 plane. In **2**, each $heen^{2-}$ is η^2:η^1:η^1:η^2:μ_3, chelating to an outer Fe and bridging to neighboring Fe atoms on either side. In **3**, each of the now six $paeo^-$ groups is η^2:η^1:η^1:μ_2, chelating to one Fe and bridging to only one neighbor. Additional bridges between outer Fe atoms are by three μ_2-OMe^- (**2**) or μ_2-OH^- (**3**) groups, and terminal ligation at three outer Fe atoms in **2** is by a Cl^- and either H_2O or MeOH. Ligation at the central Fe is completed by a terminal Cl^- ion. The main difference between **2**/**3** and prior Fe_7 disks is the tetrahedral geometry of the central Fe, which also rationalizes the near-planar Fe_6 hexagon. In both **2** and **3**, the cations are surrounded by two types of anions and by solvate molecules; the $[FeCl_4]^-$ anion in **2** forms no interactions with the cation, directly or via solvent molecules, and thus is at best only very weakly exchange-coupled to the cation.

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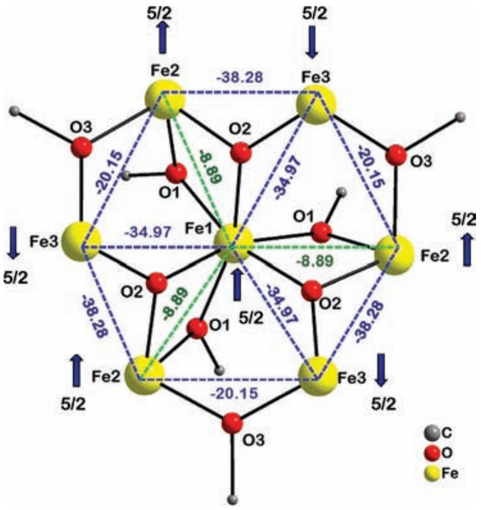

Figure 1. Core of **1** (R = Bu^t) showing the calculated *J* values (cm^{-1})[11] and resulting spin alignments giving the $S = {}^5/_2$ ground state. The frustrated interactions are the green dashed lines.

Solid-state direct-current magnetic susceptibility (χ_M) data on dried **2** and **3** were collected on microcrystallites restrained in eicosane in a 0.1 T field in the 5.0−300 K range (Figure 3). For **2**, $\chi_M T$ (with the contribution of $[FeCl_4]^-$ subtracted) increases from 29.92 cm^3 K mol^{-1} at 300 K to a maximum of 48.16 cm^3 K mol^{-1} at 50 K and then decreases to 32.83 cm^3 K mol^{-1} at 5.0 K. For **3**, $\chi_M T$ increases from 28.42 cm^3 K mol^{-1} at 300 K to a maximum of 56.71 cm^3 K mol^{-1} at 50 K and then decreases slightly to 53.10 cm^3 K mol^{-1} at 5.0 K. Both plots indicate ground-state *S* values significantly greater than $S = {}^5/_2$ for **1**: the 5.0 K value for **2** suggests $S = {}^{15}/_2$ (the spin-only value is 31.88 cm^3 K mol^{-1}), with an increase up to 50 K suggesting population of the excited states with $S > {}^{15}/_2$. The low *T* data for **3** suggests an $S = {}^{19}/_2$ or ${}^{21}/_2$ ground state (spin-only values of 49.88 and 60.38 cm^3 K mol^{-1}, respectively).

Confirmation of the ground states was obtained from fits of magnetization (*M*) data collected in the 1.8−10 K range in fields (*H*) up to 7 T. The data were fit, using the program *MAGNET*,[14] by matrix diagonalization assuming only the ground state is populated, incorporating axial anisotropy ($D\hat{S}_z^2$) and Zeeman terms, and employing a full powder average. The spin Hamiltonian is given by eq 1, where $\hat{S}_z$ is the *z*-axis spin projection, *g* is the Landé *g* factor, μ_B is the Bohr magneton, and μ_0 is the vacuum permeability.

$$\mathscr{H} = D\hat{S}_z^{\,2} + g\mu_B\mu_0\hat{S}\cdot H \qquad (1)$$

For **2**, we could not get an acceptable fit using data collected up to 7 T, a problem often caused by low-lying excited states, especially if some have an *S* value larger than the ground state. Using data collected at ≤2 T gave an acceptable fit with $S = {}^{15}/_2$, $D = -0.13$ cm^{-1}, and $g = 2.12$. For **3**, a satisfactory fit with all data was obtained with $S = {}^{21}/_2$, $D = -0.08$ cm^{-1}, and $g = 1.97$ (Figures S1−S4 in the Supporting Information, SI). These *S* values were supported by alternating-current data that gave extrapolated values at 0 K of just under 30 and 60 cm^3 K mol^{-1}, respectively (Figures S5 and S6 in the SI).

Complexes **2** and **3** thus possess much higher *S* values than prior Fe^{III}_7 disks such as **1**. A high *S* has been seen previously for Fe_7 disks only when they are Fe^{II} ($S = 10$)[15] or mixed-valent $Fe^{II/III}$ ($S = {}^{29}/_2$),[16] leading to some couplings being F. To see a high *S* in Fe^{III}_7 disks where all couplings are AF was surprising, especially because all magnetically characterized Fe^{III}_7 clusters of any structure in the literature have $S = {}^5/_2$ or less.[8,9,17,18] We thus sought its rationalization from the *J* values of **2** and **3**, obtained as for **1** (Figure 4). The main differences between **2**/**3** and **1** (Figure 1) are that all J_{io} values are now strong in the former, and all of the J_{oo} values are much weaker. Thus, the J_{oo} values are now frustrated, and the outer Fe spins are aligning more or less parallel to each other and antiparallel to the central Fe spin. The limiting situation is $S = {}^{25}/_2$ when the outer spins are perfectly parallel, and antiparallel to the central spin; **3** almost reaches this value, but the outer J_{oo} value must not be completely frustrated, and there must be some intermediate-spin alignments from the competition between J_{io} and J_{oo}. A tentative rationalization of the *S* values is provided in Figure S7 in the SI. **2** has a slightly stronger average J_{io} value than **3** but also a slightly stronger J_{oo} value, so we refrain from attempting a more detailed rationalization of their *S* values until more accurate *J* values from density functional theory calculations are available. The main conclusion for now is that these new Fe_7 disks have distinct structural differences from previous ones, primarily arising from the tetrahedral central Fe, leading to a major switch in the relative magnitude of the J_{io} vs J_{oo} plot and resulting in high ground-state *S* values from the resulting spin-frustration pattern. High spins in several other Fe^{III}_x clusters are, of course, known, but it is

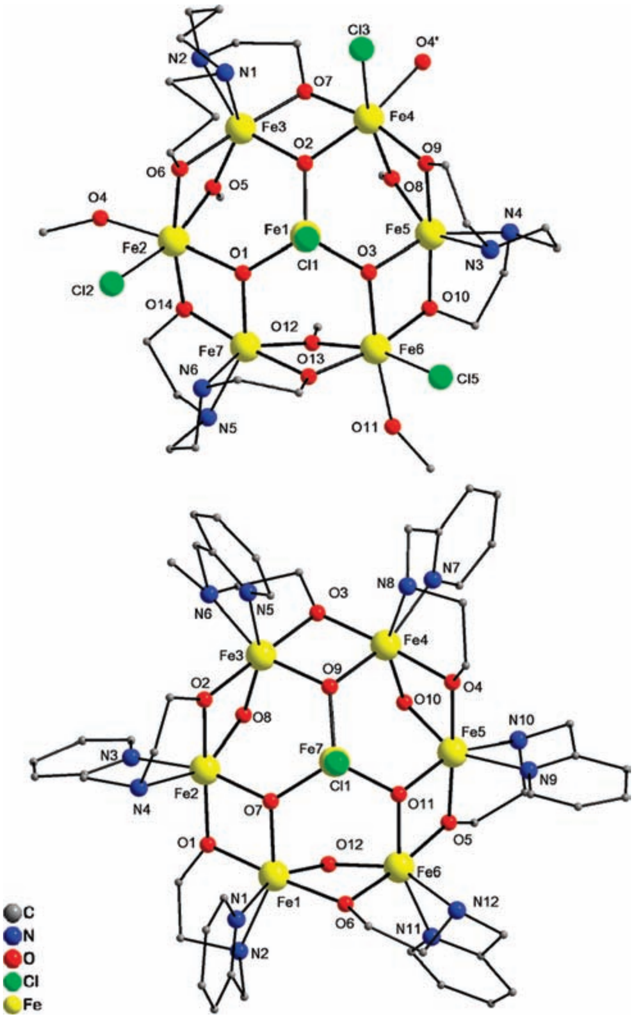

Figure 2. Structures of the cations of **2** (top) and **3** (bottom). H atoms have been removed for clarity.

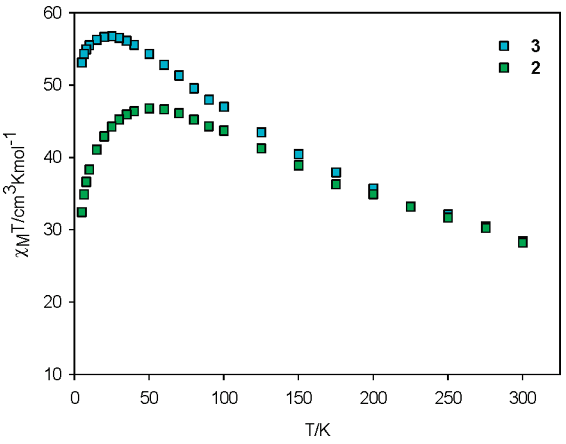

Figure 3. $\chi_M T$ vs T plots for **2** (with the $[FeCl_4]^-$ contribution subtracted) and **3** in a 0.1 T field.

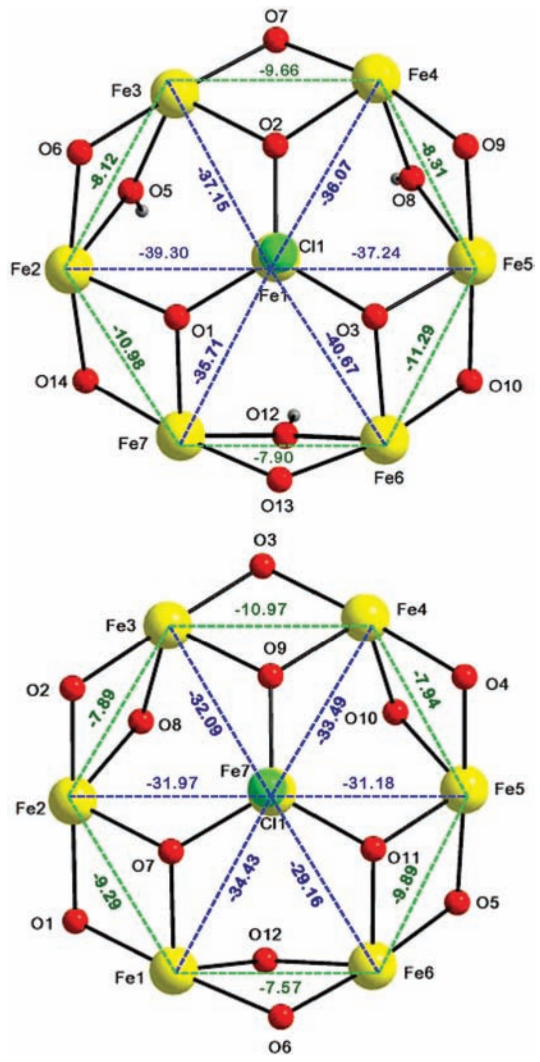

Figure 4. Cores of **2** (top) and **3** (bottom) showing the calculated J values (cm^{-1}) for each Fe_2 pair.

interesting that the present Fe_7 disks also appear to demonstrate the ability to give variable ground states,[19] which has not been seen for these other examples.[20]

Finally, preliminary ZILSH calculations on **1** have given J values comparable with those in Figure 1, supporting the validity of determining the J values of **1** via the magnetostructural correlation,[11] and by extension of those of **2** and **3**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data (CIF) and magnetism figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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