

Raising the Spin of Fe^{III}₇ Disklike Clusters: The Power of Molecular Spin Frustration

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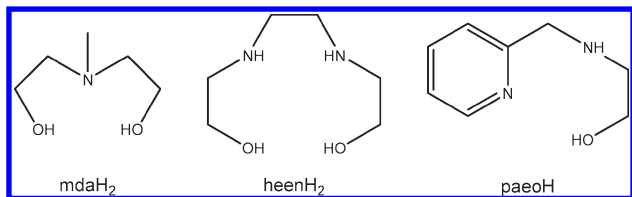
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S Supporting Information

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 Mn₇ (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 [Fe₇O₃(O₂CR)₉(mda)₃(H₂O)₃] (**1**; mdaH₂ = *N*-methyl-diethanolamine), which possesses a buckled Fe₆ loop around a central Fe atom and an $S = 5/2$ ground state.



As in our Mn₇ 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 Mn₇.^{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 Fe₇ disk while exploring Fe^{III} chemistry with *N,N'*-bis(2-hydroxyethyl)ethylenediamine (heenH₂) and 2-(2-pyridylmethyl)aminoethanol (paeoH). This gives much higher ground-state spins.

We have previously used heenH₂ in Fe chemistry but not paeoH.¹² In the present work, the reaction of FeCl₂ and heenH₂ (1:1) in refluxing MeOH gave upon cooling [Fe₇O₃(OMe)₃(heen)₃Cl_{4.5}(MeOH)(H₂O)_{1.5}]Cl_{1.25}[FeCl₄]_{1/4} (**2**), isolated as orange needles of 2·2MeOH·¹/₂H₂O in 10% nonoptimized yield after 7 days. Similarly, the reaction of Fe(ClO₄)₃, paeoH, and NEt₃ (1:3:1) in MeOH gave [Fe₇O₃(OH)₃Cl(paeo)₆](Cl)(ClO₄)₄ (**3**) as orange crystals of 3·2Me₂CO·¹/₂Et₂O in 14% nonoptimized yield. The cations of **2** and **3** have almost identical Fe₇ cores (Figure 2)¹³ consisting of a near-planar Fe^{III}₆ hexagon linked to a central Fe^{III} ion by three μ₃-O²⁻ ions and lying 1.437 Å (**2**) or 1.484 Å (**3**) above the Fe₆ plane. In **2**, each heen²⁻ is η²:η¹:η¹:η²:μ₃, chelating to an outer Fe and bridging to neighboring Fe atoms on either side. In **3**, each of the now six paeo⁻ groups is η²:η¹:η¹:μ₂, chelating to one Fe and bridging to only one neighbor. Additional bridges between outer Fe atoms are by three μ₂-OMe⁻ (**2**) or μ₂-OH⁻ (**3**) groups, and terminal ligation at three outer Fe atoms in **2** is by a Cl⁻ and either H₂O or MeOH. Ligation at the central Fe is completed by a terminal Cl⁻ ion. The main difference between **2/3** and prior Fe₇ disks is the tetrahedral geometry of the central Fe, which also rationalizes the near-planar Fe₆ hexagon. In both **2** and **3**, the cations are surrounded by two types of anions and by solvate molecules; the [FeCl₄]⁻ 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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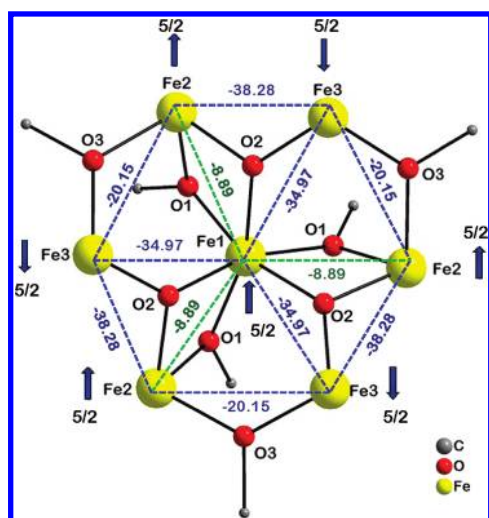


Figure 1. Core of **1** ($R = \text{Bu}^t$) showing the calculated J values (cm^{-1})¹¹ and resulting spin alignments giving the $S = 5/2$ ground state. The frustrated interactions are the green dashed lines.

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 $[\text{FeCl}_4]^-$ subtracted) increases from $29.92 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to a maximum of $48.16 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K and then decreases to $32.83 \text{ cm}^3 \text{ K mol}^{-1}$ at 5.0 K. For **3**, $\chi_M T$ increases from $28.42 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to a maximum of $56.71 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 K and then decreases slightly to $53.10 \text{ cm}^3 \text{ K mol}^{-1}$ 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 $31.88 \text{ cm}^3 \text{ K mol}^{-1}$), 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 $60.38 \text{ cm}^3 \text{ K mol}^{-1}$, 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.

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

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 $S = 15/2$, $D = -0.13 \text{ cm}^{-1}$, and $g = 2.12$. For **3**, a satisfactory fit with all data was obtained with $S = 21/2$, $D = -0.08 \text{ cm}^{-1}$, 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 $60 \text{ cm}^3 \text{ K mol}^{-1}$, 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 $\text{Fe}^{\text{II/III}}$ ($S = 29/2$),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

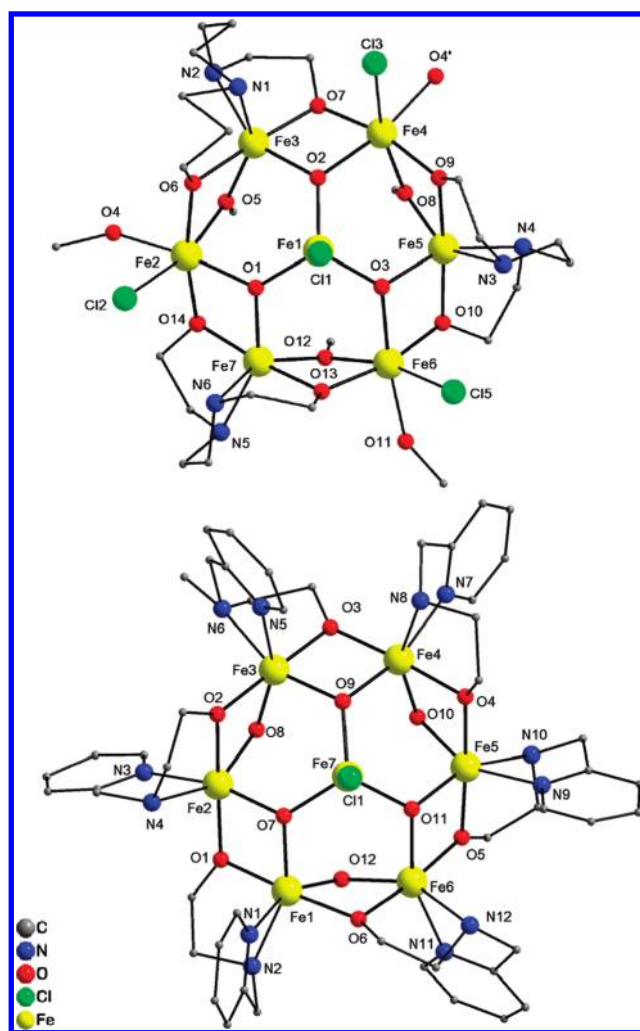


Figure 2. Structures of the cations of **2** (top) and **3** (bottom). H atoms have been removed for clarity.

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_{i0} values are now strong in the former, and all of the J_{00} values are much weaker. Thus, the J_{00} 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_{00} value must not be completely frustrated, and there must be some intermediate-spin alignments from the competition between J_{i0} and J_{00} . A tentative rationalization of the S values is provided in Figure S7 in the SI. **2** has a slightly stronger average J_{i0} value than **3** but also a slightly stronger J_{00} 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_{i0} vs J_{00} 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

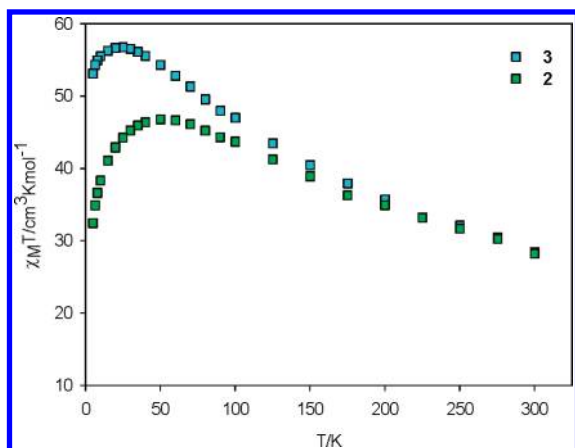


Figure 3. χ_{MT} vs T plots for **2** (with the $[\text{FeCl}_4]^-$ contribution subtracted) and **3** in a 0.1 T field.

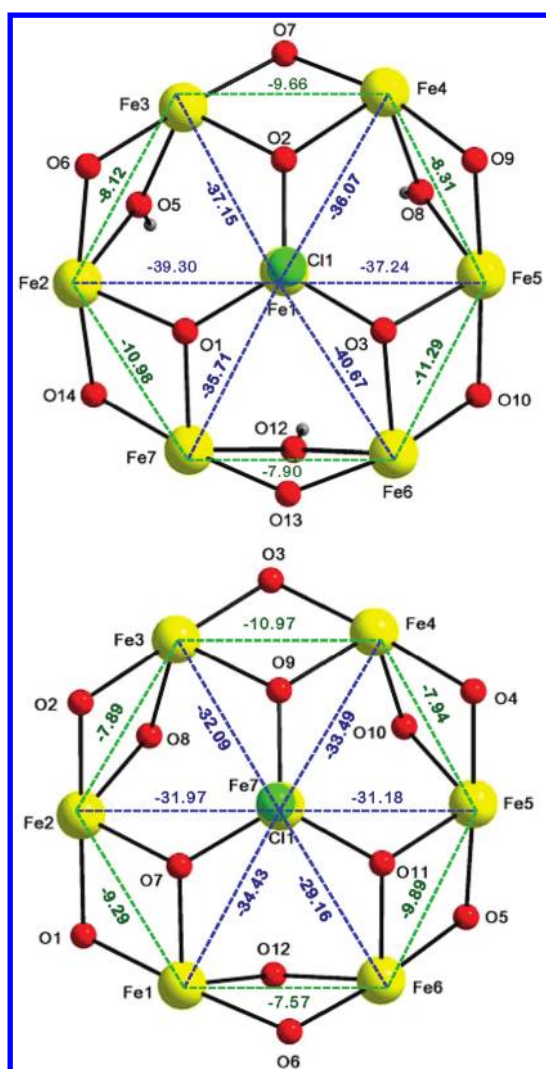


Figure 4. Cores of **2** (top) and **3** (bottom) showing the calculated J values (cm^{-1}) for each Fe_2 pair.

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

S 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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REFERENCES

- (1) Taft, K. L.; Papaefthymiou, G. C.; Lippard, S. J. *Inorg. Chem.* **1994**, *33*, 1510.
- (2) Bertini, I. G. H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
- (3) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66.
- (4) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.
- (5) Karotsis, G.; Kennedy, S.; Teat, S. J.; Beavers, C. M.; Fowler, D. A.; Morales, J. J.; Evangelisti, M.; Dalgarno, S. J.; Brechin, E. K. *J. Am. Chem. Soc.* **2010**, *132*, 12983.
- (6) Stamatos, T. C.; Poole, K. M.; Foguet-Albiol, D.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *Inorg. Chem.* **2008**, *47*, 6593.
- (7) Stamatos, T. C.; Foguet-Albiol, D.; Poole, K. M.; Wernsdorfer, W.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *Inorg. Chem.* **2009**, *48*, 9831.
- (8) Ako, A. M.; Waldmann, O.; Mereacre, V.; Klower, F.; Hewitt, I. J.; Anson, C. E.; Gudel, H. U.; Powell, A. K. *Inorg. Chem.* **2007**, *46*, 756.
- (9) Jones, L. F.; Jensen, P.; Moubaraki, B.; Berry, K. J.; Boas, J. F.; Pilbrow, J. R.; Murray, K. S. *J. Mater. Chem.* **2006**, *16*, 2690.
- (10) Datta, S.; Betancur-Rodriguez, A.; Lee, S. C.; Hill, S.; Foguet-Albiol, D.; Bagai, R.; Christou, G. *Polyhedron* **2007**, *26*, 2243.
- (11) Weihe, H.; Gudel, H. U. *J. Am. Chem. Soc.* **1997**, *119*, 6539.
- (12) (a) Bagai, R.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 12918. (b) Bagai, R.; Abboud, K. A.; Christou, G. *Chem. Commun.* **2007**, 3359.
- (13) See Supporting Information.
- (14) Davidson, E. R. Indiana University, Bloomington, IN, 1999.
- (15) Hoshino, N.; Ako, A. M.; Powell, A. K.; Oshio, H. *Inorg. Chem.* **2009**, *48*, 3396.
- (16) Oshio, H.; Hoshino, N.; Ito, T.; Nakano, M.; Renz, F.; Gutlich, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 223.
- (17) Bagai, R.; Datta, S.; Betancur-Rodriguez, A.; Abboud, K. A.; Hill, S.; Christou, G. *Inorg. Chem.* **2007**, *46*, 4535.
- (18) Khanra, S.; Konar, S.; Clearfield, A.; Helliwell, M.; McInnes, E. J. L.; Tolis, E.; Tuna, F.; Winpenny, R. E. P. *Inorg. Chem.* **2009**, *48*, 5338.
- (19) The possibility that **2** is also $S = 21/2$ and χ_{MT} decreases below 50 K due to intermolecular interactions is disfavored because it would require stronger interactions than suggested by the crystal structure.
- (20) (a) Powell, G. W.; Lancashire, H. N.; Brechin, E. K.; Collison, D.; Heath, S. L.; Mallah, T.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 5772. (b) Goodwin, J. C.; Sessoli, R.; Gatteschi, D.; Wernsdorfer, W.; Powell, A. K.; Heath, S. L. *J. Chem. Soc., Dalton Trans.* **2000**, 1835. (c) Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed.* **1984**, *23*, 77.