Magnetic Couplings in Spin Frustrated Fe$_7^{III}$ Disklike Clusters

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Supporting Information

ABSTRACT: Using a methodology based on noncollinear coupled-perturbed density functional theory [J. Chem. Phys. 2013, 138, 174115] we calculate the magnetic exchange coupling parameters in a recently synthesized set of Fe$_7^{III}$ disklike clusters [Inorg. Chem. 2011, 50, 3849–3851] to explain the unusually high ground-state spin found in the experiments. We show that the calculated exchange interactions for the new series of Fe$_7^{III}$ disks present strikingly different trends compared to prior Fe$_7^{III}$ disks. These differences are attributed to variations in the bridging ligands and the consequent structural changes in the complexes. The impact of these differences on the experimental ground-state spin of these complexes is rationalized using a simple classical spin model system and the calculated magnetic exchange couplings.

1. INTRODUCTION

Transition metal complexes featuring a large number of unpaired metal $d$ electrons are of growing interest for applications such as spintronics and magnetic memory storage. One area of interest is the design of novel molecular magnets featuring high ground-state spins $S_{tot}$ by tuning the different magnetic interactions through motivated structural perturbations. Disklike clusters such as Mn$_7$ and Fe$_7$ have attracted attention since they can feature a rich variety of spin ground-states depending on the particular competition between different $J$ interactions and spin-frustration effects. Recently, a set of Fe$_7^{III}$ disklike clusters with a six-pointed star topology were prepared by one of us (GC), given by [Fe$_7$(OMe)$_5$(heen)$_3$Cl$_{4.5}$(MeOH)(H$_2$O)$_{1.5}$][FeCl$_4$]$_{1/4}$ (shown in Scheme 1 as complex 2), and [Fe$_7$(OH)$_5$(Cl)-(paeo)$_5$][(Cl)(ClO$_4$)$_4$] (shown in Scheme 1 as complex 3), that feature an unusually large experimentally observed ground-state spin of $S_{tot} = 15/2$ and 21/2, respectively. Except a recently reported $S_{tot} = 21/2$ disk prepared by Kizas et al., typically Fe$_7^{III}$ disks with antiferromagnetic interactions yield low-spin ground-states of $S_{tot} = 5/2$. To gain insight into the origin of this unusually large spin, in this work we determine the magnetic interactions that take place in complexes 2 and 3 using Kohn–Sham density functional theory (KS-DFT). For comparison, we also consider a prior studied Fe$_7^{III}$ disklike cluster [Fe$_7$(O$_2$CR$_9$(mda)$_3$(H$_2$O)$_3$] shown in Scheme 1 as complex 1 with ground-state spin of $S_{tot} = 5/2$. For clarity, the Heisenberg–Dirac spin Hamiltonian convention we will be employing is given by

$$\hat{H}_{\text{HD}} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$  \hspace{1cm} (1)

The reported magnetic couplings in this work were calculated using a recently developed methodology based on noncollinear coupled-perturbed KS-DFT. This methodology defines and computes the $J$ couplings in terms of a Hessian of the KS energy with respect to local spin-rotation angles from the collinear high-spin (HS) reference configuration. For the purpose of making this work self-contained, we briefly remark on the relevant points of this method. To evaluate the derivative of the electronic energy with respect to local spin angles for a pair of metal atoms, we introduce the constraint condition

$$s_i \times s_j = \theta_{ij} \hat{y}$$  \hspace{1cm} (2)

where $s_i$, $s_j$ are the local-spins of the 1st and 7th metal atoms, and $1 < j \leq N$ (for the Fe$_7$ systems in this work, $N = 7$). Finding the stationary points of the Kohn–Sham energy subject to this constraint condition via Lagrange multipliers yields a modified single-particle eigenfunction problem which, assuming a collinear HS reference solution, simplifies to

$$(\hat{h} + J + V_{\text{XC}} - \sum_{i<j} \lambda_{ij} \hat{f}_{ij}) \psi_k = \epsilon_k \psi_k$$  \hspace{1cm} (3)

with

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In 3 and 4, \( \hat{h} + \hat{f} + \hat{V}_{\text{SC}} \) is the standard KS Hamiltonian, \( \lambda_{ij} \) are the Lagrange multipliers, and \( \hat{\sigma} \) are Pauli operators. Considering \( \lambda_{ij} \) to be small and solving the first-order coupled-perturbed equations for each of the perturbations, we obtain for the Fe₇ case a \( 6 \times 6 \) Hessian matrix \( [E]_{ij} = \partial^2 E_{\text{KS}} / (\partial \theta_{i} \partial \theta_{j}) \), the inversion of which gives the constraint Hessian \( [E_{\varphi}]_{ij} = \partial^2 E_{\varphi} / (\partial \theta_{i} \partial \theta_{j}) \). The magnetic couplings parameters may then be obtained by inspection of the matrix elements of the constraint Hessian via

\[
\hat{J}_{ij} = \frac{\hat{\sigma}_{i}^{x} \hat{\sigma}_{j}^{x}}{s_{i} s_{j}} \tag{4}
\]

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In the former case, \( J_{io} \) and \( J_{oo} \) can be comparable and there will be different degrees of spin-frustration. Although the formally correct way of dealing with this problem is by finding the eigenstates and eigenvalues of the quantum spin Hamiltonian, a simple inspection of the classical ground-state energy in terms of the local magnetic moment orientations can give some insight into the degree of frustration for different exchange coupling ratios \( J_{io}/J_{oo} \). It should be pointed out that classical spin models have been successfully employed to describe the magnetic properties of large Fe²¹ frustrated spin systems.²⁸ To inspect the solutions of the classical spin system, we have minimized the energy as a function of the spin orientations of the corresponding hexagonal Fe²¹ disklike core (shown in Figure 1) classical model for different \( J_{io}/J_{oo} \) ratios using a simple Monte Carlo technique. In this model, while all solutions present coplanar spin vectors, the spin-frustrated solutions are characterized by noncollinear spin vectors as shown schematically in Figure 2. In Figure 1 we show the total spin \( S_{\text{tot}} \) of the lowest-energy solutions as a function of \( J_{io}/J_{oo} \). We find that, within this model, frustrated high-spin solutions occur for \( |J_{io}| \leq 4|J_{oo}| \) while for \( |J_{io}| \geq 4|J_{oo}| \) the spin of the system saturates at the highest value \( S_{\text{tot}} = 25/2 \), as expected. High-spin solutions that give \( S_{\text{tot}} = 15/2 \) (complex 2) and \( S_{\text{tot}} = 21/2 \) (complex 3) are expected for ratios \( J_{io}/J_{oo} \approx 2.7 \) and \( J_{io}/J_{oo} \approx 3.5 \) respectively.

Now let us consider our DFT results. Beginning with complex 1, in Figure 3 we show calculated magnetic couplings (cm⁻¹) for nearest-neighbor metal atoms. For this complex, three strong antiferromagnetic interactions can be identified between outer—outer Fe atoms (Fe₂—Fe₅, Fe₃—Fe₆, and Fe₄—

Scheme 1. Structures of Complexes 1—3 (with H Atoms Removed) and Simplified Hexagon Structure for the Fe₂ Core

![Scheme 1](image)

3. RESULTS AND DISCUSSION

To rationalize the spin ground-state of these systems, let us first consider an hexagonal model for the Fe²¹ disklike core (shown at the rightmost side of Scheme 1) where by symmetry there are two unique nearest-neighbor couplings, given by \( J_{io} \) (the “outer—outer” coupling) and \( J_{io} \) (the “inner—outer” coupling), and both are assumed to be antiferromagnetic (\( J \leq 0 \) and \( J_{oo} \leq 0 \)). It is useful to consider two idealized extremes, where \( |J_{io}|/|J_{oo}| \ll 1 \), and alternatively where \( |J_{io}|/|J_{oo}| \ll 1 \). In the former case, the outer—outer interactions will dominate and a classical model will give alternating antiferromagnetic ordering for the outer Fe atoms, leaving only the central Fe atom’s spin uncanceled, yielding \( S_{\text{tot}} = 5/2 \). In the latter case the inner—outer interactions will dominate and the outer ring atoms will be spin-aligned, with the central Fe antialigned to the ring, yielding \( S_{\text{tot}} = 25/2 \). In intermediate cases the strength of \( J_{io} \) and \( J_{oo} \) can be comparable and there will be different degrees of spin-frustration. Although the formally correct way of dealing with this problem is by finding the eigenstates and eigenvalues of the quantum spin Hamiltonian, a simple inspection of the classical ground-state energy in terms of the local magnetic moment orientations can give some insight into the degree of frustration for different exchange coupling ratios \( J_{io}/J_{oo} \). It should be pointed out that classical spin models have been successfully employed to describe the magnetic properties of large Fe²¹ frustrated spin systems.²⁸ To inspect the solutions of the classical spin system, we have minimized the energy as a function of the spin orientations of the corresponding hexagonal Fe²¹ disklike core (shown in Figure 1) classical model for different \( J_{io}/J_{oo} \) ratios using a simple Monte Carlo technique. In this model, while all solutions present coplanar spin vectors, the spin-frustrated solutions are characterized by noncollinear spin vectors as shown schematically in Figure 2. In Figure 1 we show the total spin \( S_{\text{tot}} \) of the lowest-energy solutions as a function of \( J_{io}/J_{oo} \). We find that, within this model, frustrated high-spin solutions occur for \( |J_{io}| \leq 4|J_{oo}| \) while for \( |J_{io}| \geq 4|J_{oo}| \) the spin of the system saturates at the highest value \( S_{\text{tot}} = 25/2 \), as expected. High-spin solutions that give \( S_{\text{tot}} = 15/2 \) (complex 2) and \( S_{\text{tot}} = 21/2 \) (complex 3) are expected for ratios \( J_{io}/J_{oo} \approx 2.7 \) and \( J_{io}/J_{oo} \approx 3.5 \) respectively.
While the last three inner interactions are intermediate in magnitude, the outer Fe atoms as described in the previous paragraph, consistent with the experimentally observed $S_{\text{tot}} = S/2$.

In Figure 4 we show the calculated magnetic couplings (cm$^{-1}$) for complexes 2 and 3. In this case, we can broadly identify two sets of antiferromagnetic interactions: Strong couplings between the central and outer Fe atoms bridged by $\mu_2$-O$^{2-}$, and weak couplings between the outer nearest-neighbor Fe atoms. The exchange interactions for complexes 2 and 3 are similar to each other but significantly different from those of 1. In the latter system, it is the outer–outer couplings that dominates with weak inner–outer couplings, while for 2 and 3 these trends are reversed and inner–outer interactions dominate.

From the classical model system discussed before and the calculated $J$ couplings, we can straightforwardly infer that complex 2 and 3 tend toward the extreme case of $|J_{\text{io}|} \ll |J_{\text{oo}|}$, while the same ratio for complex 1 is qualitatively similar to the case $|J_{\text{io}|} \ll |J_{\text{oo}|}$ with a corresponding $S_{\text{tot}} = 25/2$, while complex 1 is the same value of $J_{\text{io}|}$ in complexes 2 and 3 than in complex 1 confirms a higher spin ground-state in 2 and 3 than in 1, in agreement with the experimentally observed trends. A closer analysis of the calculated $J_{\text{io}}$ and $J_{\text{oo}}$ couplings yields an average $J_{\text{io}}$ to average $J_{\text{oo}}$ ratio for complex 2 of 8.5, while the same ratio for complex 3 is 9.9. According to Figure 1, these $J_{\text{io}}/J_{\text{oo}}$ ratios correspond in both cases to a saturated value of $S_{\text{tot}} = 25/2$. This indicates that even though our calculated $J$ couplings can explain the high-spin observed experimentally for complexes 2 and 3, according to the classical model (Figure 1) the strong antiferromagnetic interactions might be overestimated with respect to the weak interactions. However, our DFT calculations successfully predict a higher $J_{\text{io}}/J_{\text{oo}}$ ratio for complex 3 than for complex 2, consistent with the higher $S_{\text{tot}}$ in 3 than in 2. Therefore, besides the approximations involved, our calculated couplings correctly predict the ordering of the ground-state spin of the three complexes.

Why are the exchange coupling interactions in 2 and 3 so different from those in 1? Couplings in oxo-bridged dinuclear Fe$^{3+}$ complexes are known to be dependent on both the Fe–O bond lengths and, to a lesser but still significant extent, on the Fe–O–Fe angles, and various empirical and semiempirical magnetostructural relationships have been formulated to estimate $J$ values from these parameters.$^{29,30}$ The main difference between compounds 1 and 2/3 is the coordination of the central Fe atom, which is six-coordinate with distorted octahedral geometry in 1 and four-coordinate with distorted tetrahedral geometry in 2 and 3. Since metal–ligand bond distances decrease with decreasing coordination number, if other factors are equal, it is expected that the Fe–O bond lengths to the central Fe atom will be significantly shorter in 2 and 3 than in 1. This is indeed the case, with the XRD Fe–O bond ranges being 1.987(4)–2.023(4) Å (average 2.005 Å), 1.844(4)–1.856(4) Å (average 1.849 Å), and 1.866(3)–1.885(3) Å (average 1.875 Å) for 1–3, respectively. Decreased Fe–O bond lengths to the central Fe atom in 2 and 3 will serve to increase the other Fe–O lengths in the Fe$_{7}$ core, and the net effect is expected to be an increase in $J_{\text{io}}$ and a decrease in $J_{\text{oo}}$ relative to 1. The changes in the peripheral ligands bridging the outer Fe atoms will also have an effect, primarily on $J_{\text{oo}}$. For example, it is known from studies on a family of Mn$_{7}$ clusters, which are structurally similar to the present Fe$_{7}$ clusters, that changing the identity of the peripheral ligands can have small but significant impact on the $J$ values in the magnetic core of the molecule, altering the ground-state spin from $S_{\text{tot}} = 11$ to 16.$^{29,30}$ It is also worth pointing out that there is appreciably good qualitative agreement between the calculated DFT
couplings reported herein and those determined for 1–3 from application of the magnetostructural relationship of Weihe and Güdel as reported by Mukherjee et al. 2

4. CONCLUSIONS
A novel methodology, based on linear-response density functional theory, has been employed to explain the higher ground-state spin found in two FeIII dislikle complexes (2 and 3) by evaluating their magnetic exchange coupling parameters. Our calculations reveal that the magnetic exchange interactions of the new complexes 2 and 3 are qualitatively different compared to those of the low-spin complex 1, which leads to their significantly higher ground-state spins, in agreement with experimental observations. Our analysis shows that the origin of the different trends in the couplings is due to the structural modification of the bridging ligands in the central and periphery of the disks, which results in the suppression of the strength of the antiferromagnetic interactions between the outer Fe atoms and an enhancement of the interactions between the central and outer Fe atoms.

ASSOCIATED CONTENT

Supporting Information
Geometrical structures of complexes 1, 2, and 3 used in the calculations is provided. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

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