What Determines the Spin States of Polynuclear Transition-Metal Complexes?

Grant Goodyear and Richard M. Stratt*

Department of Chemistry, Brown University
Providence, Rhode Island 02912

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One of the most striking features of multiple-metal transition-metal complexes lies in their susceptibility to significant changes in spin state with only modest structural perturbations.[1–4] In view of the ubiquity of such complexes in metalloproteins,[5] it seems important to understand the origin of these unusual magnetic properties. However, fundamentally the same kinds of interacting spin systems have proven equally stimulating to the physics community for an entirely different reason: the possibility of novel kinds of spin ordering in solids[6] (one of which may be implicated in high-temperature superconductivity).[7] What we wish to report in this communication is that one of the lessons garnered from studying the physics of quantum mechanical spin systems suffices not only to explain the origin of the variable spin states but also to provide a simple computational route to quantitative predictions of magnetic behavior in transition-metal complexes. We illustrate these ideas by applying them to two recently synthesized hexanuclear Fe compounds.[4]

The kinds of phenomenology exhibited by the polynuclear complexes can be seen in Figure 1. In each case, the metal ions are in a high-spin environment, so the systems can be thought of as collections of quantum mechanical spin-$^5/_2$ (or spin-2) spins coupled antiferromagnetically to each other. That is, the relevant Hamiltonian is approximately of the Heisenberg form

$$\hat{H} = -\sum_{\substack{j,k \\ j\neq k}} J_{jk}\hat{\mathbf{S}}_j\cdot\hat{\mathbf{S}}_k \tag{1}$$

with $\hat{\mathbf{S}}$ the spin operator for the spin on atom j and the coupling constants J_{jk} negative.[8] Given this Hamiltonian, one would expect the antialignment tendency of antiferromagnetic couplings to favor a net 0 (or at least a minimal) overall spin for the complexes, and, indeed, one often sees such results. Yet, one also finds very similar complexes with a higher net spin value. Even more dramatic examples of spin variability are seen in (FeS)$_4$ cubane complexes.[9]

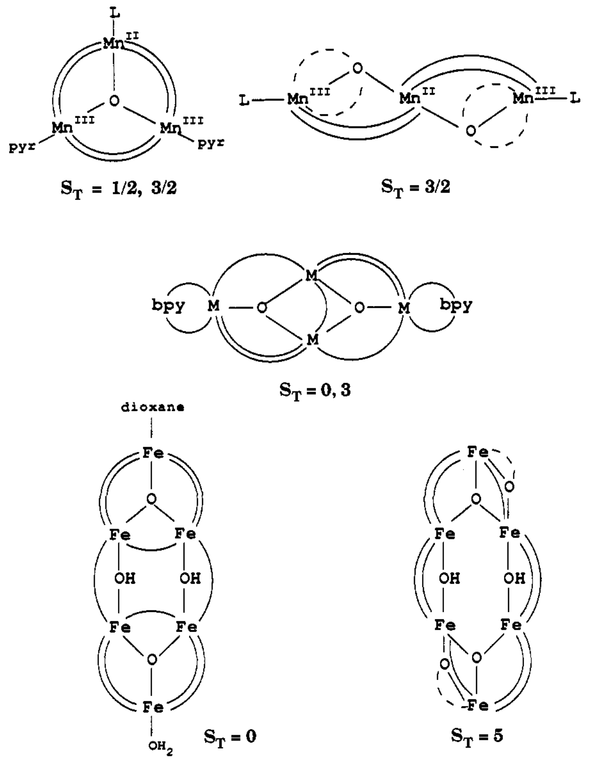

Figure 1. Sensitivity of total spin S_T to structural details in polynuclear transition-metal complexes. Upper left: **1** [Mn^{II}Mn$^{III}_2$O(O$_2$CPh)$_6$(py)$_2$-(H$_2$O)·$^1/_2$(CH$_3$CN) (S_T = $^1/_2$), **2** [Mn^{II}Mn$^{III}_2$O(O$_2$CMe)$_6$(py)$_3$]·(py) (S_T = $^3/_2$), refs 2c,d. Upper right: **3** α-Mn^{II}Mn$^{III}_2$(SALADHP)$_2$(O$_2$-CR)$_4$L$_2$ (S_T = $^3/_2$), ref 2a. Middle: **4** [Fe$^{III}_4$O$_2$(O$_2$CMe)$_7$(bpy)$_2$]-(ClO$_4$)·$^1/_4$CH$_2$Cl$_2$·H$_2$O (S_T = 0), ref 3b. **5** [Mn$^{III}_4$O$_2$(O$_2$CMe)$_7$(bpy)$_2$]-(ClO$_4$) (S_T = 3), ref 3a. Lower left: **6** [Fe$^{III}_6$O$_2$(OH)$_2$-(OH$_2$)(O$_2$CPh)$_{12}$(1,4-dioxane)] (S_T = 0), ref 4b. Lower right: **7** [Fe$^{III}_6$O$_2$(OH)$_2$(O$_2$CMe)$_{10}$(diimidazole)$_2$]·xCH$_2$Cl$_2$ (S_T = 5), ref 4a.

It is clear that the origin of the nonzero spins lies in the topology of the complexes.[1] With odd-membered rings present, spins are *frustrated*: it is mathematically impossible to satisfy the desire of every spin to be antialigned with its neighbors.[10] However, the actual spin configuration the complexes do adopt can be difficult to visualize because the number of possible quantum states grows very quickly with the size of the molecule and with the spins of the individual ions. Indeed, discerning magnetic properties by a straightforward diagonalization of eq 1 can involve a major computation; a complex with N ions, each of spin s, requires diagonalizing a $(2s + 1)^N \times (2s + 1)^N$ matrix (46 656 × 46 656 for the Fe$_6$ complexes).[4a] Nonzero-temperature properties such as the susceptibility can pose even more of a challenge.

The alternative we propose takes advantage of the fact that for large enough values of the spin, a quantum mechanical spin behaves as if it were a classical Heisenberg spin—an ordinary vector free to point in any direction in three dimensions.[11] That is, suppose we keep the Hamiltonian of eq 1 but replace the spin operators $\hat{\mathbf{S}}_j$ by the vectors $\mathbf{S}_j = S\mathbf{\Omega}_j$, with $\mathbf{\Omega}_j$ a unit vector located on the j-th metal ion. The total spin magnitude of the complex, S_T, is then defined to be the magnitude of the sum of the vectors

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[1] McKusker, J. K.; Schmitt, E. A.; Hendrickson, D. N. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991. Hendrickson, D. N. In *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing, in press.

[2] Some representative M_3 (three metal atom) complexes are described by: (a) Kessissoglou, D. P.; Kirk, M. L.; Lah, M. S.; Li, X.; Raptopoulou, C.; Hatfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 5424. (b) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244. (c) McCusker, J. K.; Jang, H. G.; Wang, S.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1874. (d) Vincent, J. B.; Chang, H. R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703.

[3] Some representative M_4 complexes: (a) Vincent, J. B.; Christmas, C.; Chang, H. R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086. (b) McCusker, J. K.; Vincent, J. B.; Schmitt, E. A.; Mino, M. L.; Shin, K.; Coggin, D. K.; Hagen, P. M.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 3012. (c) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318.

[4] Some representative M_6 complexes: (a) McCusker, J. K.; Christmas, C. A.; Hagen, P. M.; Chadha, R. K.; Harvey, D. F.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 6114. (b) Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067.

[5] Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328.

[6] See, for example: Chalker, J. T.; Holdsworth, P. C. W.; Shender, E. F. *Phys. Rev. Lett.* **1992**, *68*, 855. Sachdev, S. *Phys. Rev. B* **1992**, *45*, 12377.

[7] Anderson, P. W. *Science* **1987**, *235*, 1196.

[8] A number of more accurate Hamiltonians can easily be accommodated within the semiclassical approach described in this paper. The double-exchange term necessary for mixed-valence systems (Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423) simply requires addition of terms linear in the spin. Adding an axial field would also be straightforward, but axial fields tend to be important only at the very lowest temperatures. Indeed, since our whole approach loses its accuracy under these conditions, we omit such fields and confine our comparisons and data fittings to less extreme temperatures.

[9] Carney, M. J.; Papaefthymiou, G. C.; Spartalian, K.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6084.

[10] Toulouse, G. *Commun. Phys.* **1977**, *2*, 115.

[11] Millard, K.; Leff, H. *J. Math. Phys.* **1971**, *12*, 1000. Lieb, E. *Commun. Math. Phys.* **1973**, *31*, 327.

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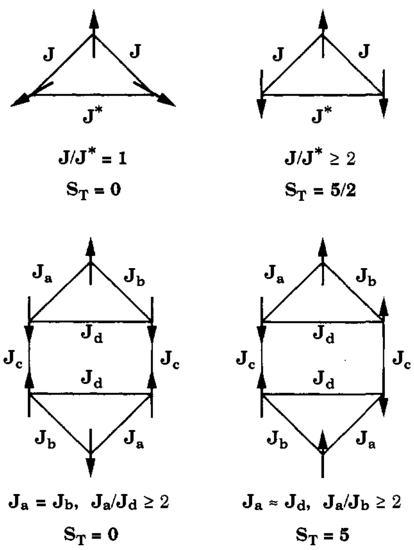

Figure 2. Classical ground-state spin configurations for trinuclear and hexanuclear complexes with spin-$^5/_2$ metal ions and the coupling constants indicated. The lower left and lower right configurations are for parameters appropriate to complexes **6** and **7**, respectively.

$\mathbf{S}_j$:

$$S_T^{\,2} = \Big(\sum_j \mathbf{S}_j\Big)^2 = \sum_{j,k} \mathbf{S}_j \cdot \mathbf{S}_k \qquad (2)$$

Hence the ground-state spin is determined by finding the arrangement of unit vectors that minimizes the energy, eq 1 (which is now a function instead of an operator). Similarly, the effective moment can be computed as a function of temperature by taking the classical ensemble average

$$\mu_{\text{eff}} = g(\langle S_T^{\,2}\rangle)^{1/2} \qquad (3)$$

with g the Landé g-factor and the ensemble average of any quantity X defined in the usual classical statistical mechanical way

$$\langle X\rangle = \int \mathrm{d}\Omega_1 \ldots \int \mathrm{d}\Omega_N\, X \exp(-\beta H)/Q$$

$$Q = \int \mathrm{d}\Omega_1 \ldots \int \mathrm{d}\Omega_N \exp(-\beta H) \qquad (4)$$

Here $\beta = 1/(k_B T)$, and each unit vector is to be integrated over 4π steradians.

These formulas are only exact in the limit that the individual atomic spins become infinite.[11] However, the surprising observation is that they turn out to be *quantitatively* accurate for the not-all-that-large spins s relevant to high-spin transition-metal ions, provided that one identifies S, the magnitude of the classical vectors, as s itself for computing the total spin and as $[s(s+1)]^{1/2}$ when computing the effective moment.[12]

Typical predictions of this model for ground states are shown in Figure 2 for some high-spin Fe$^{\text{III}}$ ($s = {}^5/_2$) complexes. It is easy to show analytically that the model leads to differing ground-state spins with just minor modifications to the ratios of coupling constants. In fact, one can understand the findings qualitatively by examining the minimum-energy orientations of the classical vectors. The triangular case, for example, switches from having three coplanar spins at 120° angles, through a succession of intermediate angles, to a two-spins-down, one-spin-up motif when the sum of favorable ↓↑ + ↑↓ energies becomes sufficiently larger than the unfavorable ↓↓ energy.[13] Similarly, the hexanuclear case can either be, or not be, dominated by the energetics of the spins around the central rectangle, depending on the coupling constant ratios.

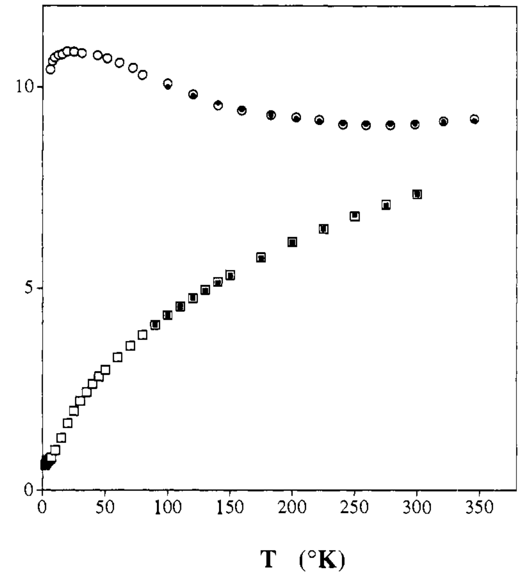

Figure 3. Temperature dependence of the effective magnetic moment (in units of μ_B) for hexanuclear complexes **6** (□) and **7** (○). Open symbols are experimental data (refs 4b and 4a, respectively), and the filled symbols are theoretical predictions based on the classical model using $g = 1.94\mu_B$ (ref 4a) and Hamiltonian parameters fit to data above 90 K (see ref 8): In cm^{-1}, ($-J_a$, $-J_b$, $-J_c$, $-J_d$) = (35.9 ± 0.1, 35.9 ± 0.1, 12.6 ± 0.2, 15.0 ± 0.02), and (35.0 ± 0.05, 5.53 ± 0.25, 12.5 ± 0.09, 33.6 ± 0.02) for **6** and **7**, respectively. The J's are labeled as in Figure 2.

The ground-state predictions of the classical model are in remarkable agreement with the experimental magnetic measurements, not only for the complexes portrayed in Figure 2 but also for the other complexes displayed in Figure 1. Using the literature values of the coupling constants for complexes **1**–**5**, one finds the measured and calculated ground-state spin values to be ($^1/_2$, 1.11), ($^3/_2$, $^3/_2$), ($^3/_2$, $^3/_2$), (0, 0), and (3, 2.67), respectively.[2a,c,d,3a,b,4] Susceptibility studies had also been performed on the hexanuclear examples, but the sheer size of the quantum mechanical problem had precluded any previous determination of the coupling constants.[4a] However, since it is straightforward to evaluate the (12-dimensional) integrals in eq 4 repeatedly by Monte Carlo methods,[14] we were able to determine the coupling constants by a Levenberg–Marquardt[15] least-squares fit of the experimental data to eq 4. Besides giving the correct ground-state spins, the fits, shown in Figure 3, indicate the usefulness of the classical model for understanding the spin system thermodynamics—and the inappropriateness of a picture based on simple ↑ and ↓ spin-$^1/_2$ spins.

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(12) This prescription defines the semiclassical (large spin) limit, but one can systematically improve on this limit by computing a coherent-state path integral. See, for example: Einarsson, T.; Johannesson, H. *Phys. Rev. B* **1991**, *43*, 5867. Note also that for mixed-valence compounds, the effective spin S on each metal atom is taken to be the value appropriate to that atom's own spin s.

(13) Yamaguchi, K. *Chem. Phys. Lett.* **1975**, *30*, 288. This paper actually applies the semiclassical approach to a low-spin, triangular, organic radical.

(14) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987; pp 131–134. The integrations here were performed by discarding the first 10^3 passes through the system and then averaging over 4×10^4 configurations, each separated by 10 passes. This procedure made Monte-Carlo fluctuations in the susceptibility at any given temperature negligible. The errors reported are χ^2 90% confidence limits derived from the fits to the experimental data.

(15) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN*, 2nd ed.; Cambridge University Press: Cambridge, 1992; Chapter 15.