The syntheses, crystal structures, and magnetic characterizations of three new hexanuclear iron(III) compounds are reported. Known \([\text{Fe}_6\text{O}_2\text{(OH)}\text{(O}_2\text{CBu})_{10}\text{(hep)}_2]\) (1) is converted to new \([\text{Fe}_6\text{O}_2\text{(OH)}\text{(O}_2\text{CBu})_9\text{(hep)}_4]\) (3) when treated with an excess of 2-(2-hydroxyethyl)-pyridine (hepH). Similarly, the new compound \([\text{Fe}_6\text{O}_2\text{(OH)}\text{(O}_2\text{CPh})_{10}\text{(hep)}_2]\) (2), obtained from the reaction of \([\text{Fe}_3\text{O}\text{(O}_2\text{CPh})_6\text{(H}_2\text{O})_3]\) with hepH, is converted to \([\text{Fe}_6\text{O}_2\text{(OH)}\text{(O}_2\text{CPh})_9\text{(hep)}_4]\) (4) when treated with an excess of hepH. This can be reversed by recrystallization from MeCN. The cores of the four \(\text{Fe}_6\) complexes all comprise two triangular \([\text{Fe}_3\text{(\text{O}_2\text{CR})_3}\text{(hep)}]^3\) units connected at two of their apices by two sets of bridging ligands. However, 1 and 2 differ slightly from 3 and 4 in the precise way the two \(\text{Fe}_3\) units are linked together. In 1 and 2, the two sets of bridging ligands are identical, consisting of one \(\mu\)-hydroxo and two \(\mu\)-carboxylate groups bridging each \(\text{Fe}_2\) pair, i.e., a \((\mu\text{-OH}^-)(\mu\text{-O}_2\text{CR}^-)^2\) set. In contrast, 3 and 4 have two different sets of bridging ligands, a \((\mu\text{-OH}^-)(\mu\text{-O}_2\text{CR}^-)^2\) set as in 1 and 2, and a \((\mu\text{-OR}^-)(\mu\text{-O}_2\text{CR}^-)^2\) set, where \(\text{RO}^-\) refers to the alkoxide arm of the hep- chelate. Variable-field and temperature dc magnetization measurements establish that 1 and 2 have \(S = 5\) ground states and significant and positive zero-field splitting parameters \((D)\), whereas 3 and 4 have \(S = 0\) ground states. This dramatic difference of 10 unpaired electrons in the ground state \(S\) values for near-isomeric compounds demonstrates an acute sensitivity of the magnetic properties to small structural changes. The factors leading to this have been quantitatively analyzed. The semiempirical method ZILSH, based on unrestricted molecular orbital calculations, was used to obtain initial estimates of the \(\text{Fe}_2\) pairwise exchange interaction constants \((J)\). These calculated values were then improved by fitting the experimental susceptibility versus \(T\) data, using a genetic algorithm approach. The final \(J\) values were then employed to rationalize the observed magnetic properties as a function of the core topologies and the presence of spin frustration effects. The large difference in ground state spin value was identified as resulting from a single structural difference between the two types of complexes, the different relative dispositions (cis vs trans) of two frustrated exchange pathways. In addition, use of the structural information and corresponding \(J\) values allowed a magnetostructural correlation to be established between the \(J\) values and both the \(\text{Fe}--\text{O}\) bond distances and the \(\text{Fe}--\text{O}--\text{Fe}\) angles at the bridging ligands.

**Introduction**

The last two decades have witnessed an explosive growth in the interest in polynuclear iron(III) compounds with primarily oxygen-based ligation. This has been mainly due to their relevance to two fields, bioinorganic chemistry and molecular magnetism. Iron--oxo centers are found in several non-heme metalloproteins. Hemerythrin, ribonucleotide reductase, and methane monoxygenase are examples of enzymes with di-iron metallosites,\(^1\) whereas the protein ferritin, responsible for iron storage, can accommodate up to \(~4500\) iron ions in an iron(oxide)/hydroxide core.\(^2\) In the magnetism area, high spin iron(III) ions have a relatively large number of unpaired electrons \((d^5, S = \frac{5}{2})\) that normally
undergo strong, antiferromagnetic exchange interactions within multinuclear iron–oxygen clusters. With high enough Fe₆ nuclearities and appropriate topologies, these compounds can sometimes possess large ground state spin (S) values, and can even occasionally function as single-molecule magnets (SMMs).³ SMMs are molecules that display slow magnetization relaxation rates and which, below a certain (“blocking”) temperature (Tₐ), can function as single-domain magnetic particles of nanoscale dimensions.⁴ In order to be a SMM, a molecule has to fulfill two conditions: It must possess both a ground state with a large spin S, and a significant anisotropy of the easy-axis (Ising) type, as reflected in a large and negative zero-field splitting parameter, D. Although the interactions between Fe³⁺ centers are normally antiferromagnetic, certain Fe₆ topologies result in large spin ground states because of the occurrence of spin frustration effects. Spin frustration is defined here in its general sense as the occurrence of competing exchange interactions of comparable magnitude that prevent (frustrate) the preferred spin alignments.⁵ For example, in certain topologies the spins of two antiferromagnetically coupled metal ions (or other spin carriers) may be forced into a parallel alignment by other, stronger interactions; thus, the intrinsic preference of the spins to align antiparallel is frustrated. An appropriate quantity and distribution of frustrated exchange pathways in some Fe₆ topologies can lead to a significantly large value of the total molecular spin, even when all the pairwise Fe² exchange interactions are antiferromagnetic.

In this paper, we describe the syntheses, structures, and properties of two Fe₆ complexes with S = 5 ground states, [Fe₆O₂(OH)₂(O₂CR)₁₀(hep)₂] (R = Bu² (1), Ph(2)), where hep⁻ is the anion of 2-(2-hydroxyethyl)pyridine. A different crystal form of 1 has been previously reported,⁶ whereas its structural analogue 2 is new. Reaction of 1 and 2 with an excess of hepH affords two new compounds: [Fe₄O₆(OH)₂(hep)₁₂](O₂CR)₇(hep)₄] (R = Bu² (3), Ph (4)), with a new type of structure, although similar to that of 1 and 2. The transformation, which involves the replacement of only two bridging ligands, dramatically changes the ground state spin from S = 5 to S = 0. We describe the quantitative rationalization of this difference using the results of semiempirical molecular orbital calculations using the recently formulated ZILSH method.⁷ These provided initial estimates of all the Fe–Fe exchange constants (J), which were then refined by fitting their values to reproduce the experimental variable-temperature magnetic susceptibility of the complexes. The final J values not only correctly predict the observed S = 0 vs S = 5 spin ground states, but quantitatively rationalize how they come about. Finally, we also describe a magnetostructural correlation between these J values and both the average Fe–O distances and the Fe–O–Fe angles through the shortest Fe–O–Fe pathway of interaction. This should prove extremely useful in the future for predicting and/or rationalizing the magnetic properties of new multinuclear Fe(III) complexes, and how those properties might be affected by relatively small structural changes.

**Experimental Section**

**Syntheses.** All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. [Fe₂O₂(OH)₂(O₂CBu)₁₀(hep)₁₂] (1) and [Fe₂O₂(OH)₂(O₂CPh)₁₀(hep)₁₂]²⁻ were prepared as described in the literature; hepH is 2-(2-hydroxyethyl)pyridine.

[Fe₂O₂(OH)₂(He₄)] (H₂O)₃. A stirred solution of FeCl₃·4H₂O (3.00 g, 15.1 mmol) and sodium benzoate (6.52 g, 45.3 mmol) in water (60 mL) was treated with a solution of benzoic acid (11.1 g, 90.5 mmol) in acetonitrile (60 mL). The mixture was boiled for 30 min and then cooled to room temperature. The resulting precipitate was collected by filtration and washed with a copious amount of water and a little acetonitrile, in which the compound is partially soluble. The material was vacuum-dried; yield, 69%. Anal. Calcd (Found) for C₄₂ H₃₆ Fe₃ O₁₆: C, 52.31 (52.47); H, 3.76 (3.56)%.

[Fe₂O₂(OH)₂(He₄)] (H₂O)₃. A stirred solution of Fe(NO₃)₃·9H₂O (1.6 g, 5.8 mmol) in water (20 mL) was treated with a solution of sodium benzoate (3.5 g, 24 mmol) in water (30 mL). A light orange precipitate was obtained immediately. The solid was collected by filtration, washed with copious amounts of water and dried under vacuum; yield, 82%. Selected IR data (KBr, cm⁻¹): 3408(br); 3062(m); 1700(m); 1601(s); 1564(s); 1410(vs); 1177(m); 1070(m); 1025(m); 1002(w); 940(w); 840(w); 818(w); 721(s); 673(s); 593(m); 464(s).

[Fe₂O₂(OH)₂(He₄)] (H₂O)₃. A stirred solution of Fe(NO₃)₃·9H₂O (1.6 g, 5.8 mmol) in water (20 mL) was treated with a solution of sodium benzoate (3.5 g, 24 mmol) in water (30 mL). A light orange precipitate was obtained immediately. The solid was collected by filtration, washed with copious amounts of water and dried under vacuum; yield, 82%. Selected IR data (KBr, cm⁻¹): 3408(br); 3062(m); 1700(m); 1601(s); 1564(s); 1410(vs); 1177(m); 1070(m); 1025(m); 1002(w); 940(w); 841(w); 819(w); 717(s); 686(m); 675(m); 631(m); 484(s).


**Structurally Related Fe₆ Molecular Clusters**

Anal. Calcd (Found) for C₈₄H₆₈Fe₆N₂O₂₆: C, 54.34 (53.81); H, 3.69 (3.55); N, 1.51 (1.58)%. Selected IR data (KBr, cm⁻¹): 3440(br); 2923(vw); 2888(vw); 2854(w); 1598(s); 1554(s); 1527(m); 1492(m); 1405(vs); 1314(v); 1251(w); 1177(m); 1157(w); 1113(w); 1082(m); 1068(m); 1026(m); 718(s); 689(m); 673(m); 661(m); 595(m); 538(m); 474(s), 430(m).

**Method A**. A solution of [Fe₆O(O₂CPh)₉(H₂O)₃][NO₃] (0.20 g, 0.19 mmol) in hot acetonitrile (15 mL) was treated with hepH (72 mg, 0.57 mmol) in acetonitrile (3 mL). The solution mixture was stirred and heated for several hours, after which it was filtered hot and the filtrate left undisturbed for several days at room temperature. The resulting crystals were collected by filtration and washed with acetonitrile; yield, 31%.

**Method B**. Compound 4 (0.1 g, 0.05 mmol) was stirred in hot acetonitrile (15 mL) for several hours. The very pale orange solution was then filtered hot to remove undissolved starting material, and the filtrate was allowed to cool slowly to room temperature. Crystals of 2 formed over several hours, and these were collected by filtration and washed with acetonitrile. The product was identified by IR comparison with material from method A.

**Method C**. A solution of [Fe₆O(O₂CBu)₉(hep)] (0.20 g, 0.11 mmol) in MeCN (3 mL). The solution was boiled gently for 10 min and then treated with a solution of hepH (72 mg, 0.57 mmol) in acetonitrile (3 mL). These were collected by filtration and washed with acetonitrile; yield, 31%.

**Method A.** The product was identified by IR comparison with material from method A.

**Method B.** A solution of [Fe₆O(O₂CPh)₉(H₂O)₃][NO₃] (0.20 g, 0.11 mmol) in hot acetonitrile (15 mL) was treated with hepH (72 mg, 0.57 mmol) in acetonitrile (3 mL). The solution was boiled gently for 10 min and then treated with a solution of hepH (72 mg, 0.57 mmol) in acetonitrile (3 mL). These were collected by filtration and washed with acetonitrile; yield, 31%.

**Table 1.** Crystallographic Data for [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (1), [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (2), [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (3), and [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (3)-MeCN (4·3MeCN)

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<th>Comps</th>
<th>CmH₁₆Fe₆-</th>
<th>CmH₂₁N₂O₆</th>
<th>CmH₂₁N₂O₆</th>
<th>Cm₁₆H₁₆N₂O₃·Fe₆N₂O₂₃</th>
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<td>4.6(12.1)</td>
<td>4.74(11.1)</td>
<td>5.59(15.8)</td>
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</table>

*Refined by full-matrix least-squares cycles. Data collection parameters and structure solution and refinement details are listed in Table 1.*

The new crystalline form of [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (1) with no solvent of crystallization was obtained by slow evaporation of a saturated solution in dichloromethane. The compound crystallizes in the monoclinic space group P2₁/c. The structure is centrosymmetric with the asymmetric unit containing half of the Fe₆ complex. A direct-methods solution was calculated that located all non-hydrogen atoms from the electron density map, and these were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated, ideal positions and refined as riding atoms with isotropic displacement parameters set to be a multiple of that of the parent atom. The final full-matrix least-squares refinement on F² converged to R = 5.34% (I = 2(I)) and wR2 = 14.29% (all data). The remaining electron density is located around the Fe atoms. One of the Bu groups is disordered over two positions, which refined to 54% and 46% occupancies.

**Table 1.** Crystallographic Data for [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (1), [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (2), [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (3), and [Fe₆O(OH)₂(O₂CPh)₉(hep)][j] (3)-MeCN (4·3MeCN)

- **Inorganic Chemistry,** Vol. 43, No. 18, 2004
- **(10) SHELXL-Plus V5.10; Bruker Analytical X-ray Systems: Madison, WI.**
again placed in ideal positions and refined with isotropic displacement parameters, except for H3, which is involved in a strong hydrogen bond with O25 and was refined for all parameters. The final full-matrix least-squares refinement on \( F^2 \) converged to \( R_1 = 4.74\% \) (\( I > 2\sigma(I) \)) and \( wR_2 = 11.1\% \) (all data). Remaining electron density and large displacement parameters for several methyl groups and the second nonchelating hep group suggest some further, unresolved disorder. Attempts to refine such disorders did not yield any improvement in the final residuals and thermal parameters.

\[
[\text{Fe}_6\text{O}_2\text{OH}(\text{O}_2\text{CPh})_9(\text{hep})_4][\text{3MeCN}(4\cdot3\text{MeCN})] \text{ crystallizes in the triclinic space group P1.} \]

The asymmetric unit contains one \( \text{Fe}_6 \) molecule and three molecules of solvent. A structure solution by direct methods located most of the non-hydrogen atoms; the remaining non-hydrogen atoms were located by full-matrix least-squares and difference Fourier map cycles. Non-hydrogen atoms were refined using anisotropic displacement parameters, whereas all hydrogen atoms were placed in ideal positions and refined with isotropic displacement parameters riding on those of the parent atom. The crystal exhibits two kinds of disorder. First, disordered acetonitrile molecules were found in a solvent channel; second, a nonchelating hep molecule is disordered with a hydroxide group (84% and 16%, respectively), hydrogen-bonded to an acetonitrile molecule. The figures and calculations described in this paper refer to the majority species, i.e., when the bridging group is hep. The final full-matrix least-squares refinement on \( F^2 \) converged to values of \( R_1 \) and \( wR_2 \) of 5.59% (\( I > 2\sigma(I) \)) and 15.8% (all data), respectively. The final difference Fourier map shows remaining electron density near the disordered hep molecule, indicating that additional solvent molecules (most likely water) may be involved in the disorder.

**Computational Methods.** The exchange interactions in 1–4 were calculated using the recently developed semiempirical ZILSH method.\(^7,11\) The method uses molecular orbital (MO) calculations with the intermediate neglect of differential overlap Hamiltonian parametrized for optical spectroscopy (INDO/S) of Zerner\(^12,13\) to obtain energies for various alignments of the spins of the metal ions in a polynuclear transition metal complex. A semiempirical application\(^ \ldotp 11\) of Davidson’s local spin operator\(^14,15\) was used to obtain spin couplings between metal ions, \( \langle \hat{S}_A \hat{S}_B \rangle \), from the semiempirical wave functions. Together with the energies, these quantities were used to obtain estimates of the exchange constants \( J_{AB} \) that appear in the Heisenberg spin Hamiltonian (HSH) of eq 1

\[
\hat{H} = \hat{H}_0 - 2 \sum_{A \neq B} J_{AB} \hat{S}_A \cdot \hat{S}_B \tag{1}
\]

where \( \hat{H}_0 \) contains all spin-independent terms. The HSH gives the energies of the spin states of the complex as in eq 2

\[
E_i = E_0 - 2 \sum_{A \neq B} J_{AB} \langle \hat{S}_A \hat{S}_B \rangle \tag{2}
\]

where \( E_0 \) contains spin-independent contributions to the energy, such as electron–nuclear attractions. Given the energies and spin couplings of a number of spin components equal to the number of parameters \( J_{AB} \) and \( E_0 \), eq 2 can be solved simultaneously for the parameter values.

The large size and complex electronic structure of polynuclear transition metal complexes makes the application of a basis of spin states prohibitive. Instead of spin state wave functions that are linear combinations of many determinants, ZILSH uses single determinant wave functions, composed of a single set of MOs. The MOs are optimized with the unrestricted Hartree–Fock self-consistent field (UHF-SCF) formalism.\(^9,10\) The local spin operator allows expectation values \( \langle \hat{S}_A \hat{S}_B \rangle_{\text{UHF}} \) to be computed for the MO wave functions. Under certain conditions (discussed below),\(^9\) the energies of the MO wave functions are given by eq 2 with \( \langle \hat{S}_A \hat{S}_B \rangle_{\text{UHF}} \) and the same exchange constants that describe the true spin states of the system. This means that the exchange constants obtained are of comparable accuracy regardless of the total spin of the wave function (see ref 7 for discussion). For complexes of modest size, the energies and compositions of the spin states can be examined by substituting the exchange constants into the HSH and diagonalizing in a basis of components \( |S_A M_A \rangle |S_B M_B \rangle |S_C M_C \rangle \), where \( S_A \) and \( M_A \) are, respectively, the spin and z-component of spin for metal center A (e.g., \( S_A = \frac{3}{2} \) for high spin \( \text{Fe}^{3+} \) ions).

Exchange constants found with ZILSH contain errors due to using approximate UHF wave functions rather than spin states, and errors in energies inherent in the semiempirical parametrization of the INDO/S method. Considering the former, it has been demonstrated that if the single determinant wave functions are high spin eigenfunctions of the local spin operators for the metal center spins, then the correct exchange constants are obtained regardless of the total spin of the wave function. In practice, UHF wave functions rarely meet this requirement. The size of this error can be judged in two ways. First, the expectation values of local spin for the metal centers can be compared to what would be obtained for high spin metal centers. In the case of \( \text{Fe}^{3+} \) ions, for example, the local spin quantum number is \( S_A = \frac{3}{2} \), so the expectation value \( \langle \hat{S}^z_A \rangle = S_A \left( S_A + 1 \right) \) would be 8.75. Second, the expectation value of the total spin operator, \( \langle \hat{S}^z \rangle_{\text{UHF}} \), can be compared to the value expected for single determinant wave functions in which the local spin operators for the metals have high-spin eigenvalues. This expectation value, \( \langle \hat{S}^z \rangle_{\text{L,S}} \), is given by eq 3.

\[
\langle \hat{S}^z \rangle_{\text{L,S}} = M^2 + M_{\text{max}} \tag{3}
\]

Both of these measures are used to assess the accuracy of the exchange constants obtained for complexes 1, 2, 3, and 4.

Even when the error due to using approximate wave functions is small, the error inherent in the INDO/S parameters remains. Consequently, a genetic algorithm method for refining the exchange constants to better reflect experimental data was implemented.\(^7\) This method uses the Van Vleck equation\(^17\) to relate the product of the magnetic susceptibility and temperature to the exchange constants, as described elsewhere.\(^7\) The exchange constants, electronic g factor, and temperature-independent paramagnetism (TIP) are all adjusted simultaneously to minimize the differences between experimental and calculated values of \( \chi_m T \) for temperatures above 25 K. Lower temperatures are excluded because other factors such as zero-field splitting of low-lying states (which are not obtained from the calculations) and intermolecular interactions become operative below 25 K. Exchange constants calculated with ZILSH are used

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as starting guesses, and the g factor is allowed to vary between 1.90 and 2.00. Similarly, the TIP is allowed to vary between 0.90 and 2.00. Similarly, the TIP is allowed to vary between 900 and 1200 as starting guesses, and the g factors for complexes 1, 2, 3, and 4, we use the more compact notation \( M_i M_j \ldots M_N \) to represent a component.

Two other quantities are important for analyzing spin alignments in the spin states. One is the expectation value of the \( z \)-components of spin of the metal centers, \( \langle S_i \rangle \), which are a direct indication of spin alignments. The other is the expectation value of the \( z \)-components of spin of the metal centers, \( \langle S_i \rangle \), that appears in the HSH (not to be confused with the similar quantity computed for a UHF component, discussed above), which is useful for examining spin alignments in singlet states, where all \( \langle M_i \rangle \) are zero. Also, \( \langle S_i \rangle \) is useful for analyzing spin frustration effects because it represents the actual alignment of the spins of metal centers A and B in the spin state (whereas \( j \) indicates the preferred alignment), and is positive and negative for parallel and antiparallel alignment, respectively. Thus, if \( \langle S_i \rangle \) and \( J_{AB} \) differ in sign, the A→B pathway is frustrated. In a more quantitative sense, the product \(-2 J_{AB} \langle S_i \rangle\) represents the contribution made by the A→B pathway to the total energy of the spin state. If they have different signs (i.e., if the interaction is frustrated), the total energy is increased by the interaction of spins. The product \(-2 J_{AB} \langle S_i \rangle\) was used to identify frustrated pathways in complexes 1, 2, 3, and 4.

One caveat regarding the method just described is that there are more spin components than parameters for complexes with more than three metals. In the case of the Fe₆ complexes considered here, for example, there are 32 unique ways of reversing spins of the metals, while there are only 16 parameters \( J_{AB} \) and \( E_0 \). A question that naturally arises is if the same exchange constants are obtained for different choices of spin components. This has not yet been examined in detail, but it was found by trial and error that very similar values of the parameters were obtained for different choices for the complex \[ \text{Fe}_6 \text{O}_2 \text{OH}_2 \text{(O}_2 \text{CPh}_2 \text{)}_{10} \text{(hep)}_2 \text{]} \text{[16,18,22]}. \]

Additionally, it has been demonstrated that if the component wave functions are high spin eigenfunctions of the local spin operators for the metal center spins (a condition approximately met by the wave functions found in this work, vide infra), the exchange constants found from any set of spin components are formally equivalent. See ref 7 for a detailed discussion of this question.

Other Studies. Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet model 5100 FTIR spectrophotometer in the 4000–400 cm⁻¹ range. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Series II analyzer. Magnetic measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Pascal’s constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility \( \chi_M \).

Results and Discussion

Syntheses. For convenience, the various preparations and transformations described below are summarized in Scheme 1.

We recently reported elsewhere⁶ the preparation of \[ \text{Fe}_6 \text{O}_2 \text{OH}_2 \text{(O}_2 \text{CPh}_2 \text{)}_{10} \text{(hep)}_2 \text{]} \text{(1)} \) from the reaction of \[ \text{Fe}_6 \text{O}_2 \text{CPh}_2 \text{Cu}_2 \text{(H}_2 \text{O})_3 \text{(NO}_3 \text{)} \text{]} \text{with 3 equiv of hepH. An analogous procedure was employed here to synthesize} \[ \text{Fe}_6 \text{O}_2 \text{OH}_2 \text{(O}_2 \text{CPh}_2 \text{)}_{10} \text{(hep)}_2 \text{]} \text{(2)} \). Thus, \[ \text{Fe}_6 \text{O}_2 \text{CPh}_2 \text{Cu}_2 \text{(H}_2 \text{O})_3 \text{(NO}_3 \text{)} \text{]} \text{was dissolved in hot acetonitrile and treated with 3 equiv of hepH to yield red crystals of 2 upon cooling. The reaction is summarized in eq 5: note that both the ligand hepH and the released PhCO₂⁻ groups can act as proton acceptors to facilitate formation of OH⁻ and hep⁻ groups.}

\[ 2 \text{Fe}_6 \text{O}_2 \text{OH}_2 \text{(O}_2 \text{CPh}_2 \text{)}_{10} \text{(hep)}_2 \text{]} + 4 \text{hepH} \rightarrow \text{[Fe}_6 \text{O}_2 \text{OH}_2 \text{(O}_2 \text{CPh}_2 \text{)}_{10} \text{(hep)}_2 \text{]} + 2 \text{hepH}_2^+ + 2 \text{PhCO}_2^+ + 4 \text{H}_2 \text{O} \quad (5) \]

Similar results were obtained when neutral \[ \text{Fe}_6 \text{O}_2 \text{CPh}_2 \text{Cu}_2 \text{(H}_2 \text{O})_3 \text{]} \text{was employed as the starting material. This complex is mixed valent (Fe}^{II/II}\text{Fe}^{III}), but air oxidation proved sufficient to yield the all-Fe}^{III} \text{product in high yield (49%). Although there is no easy way to study the mechanism of formation of 1 and 2, their structures suggest that the hep⁻ groups have (18) McCusker, J. K.; Christmas, C. A.; Hagen, P. M.; Chadha, R. K.; Jarvey, D. F.; Hendrickson, D. N. J. Am. Chem. Soc. 1991, 113, 6114.
induced a dimerization of two \([\text{Fe}_3(\mu_3-O)]\) units with little change to the individual \([\text{Fe}_3(\mu_3-O)]\) cores.

When complexes 1 and 2 were treated in acetonitrile with an excess of hepH, the latter was incorporated into one of the two inter-Fe\(_3\) connections between vertices. Two hep\(^-\) groups, which employ their alkoxide arms to bridge, replace a \(\mu\)-carboxylate group and the \(\mu\)-hydroxide groups, the N atoms of these hep\(^-\) ligands remaining uncoordinated. It is interesting that extra hep\(^-\) groups are only incorporated into one of the inter-Fe\(_3\) sets of bridging ligands. The conversion is summarized in eq 6.

\[
\begin{align*}
[\text{Fe}_6\text{O}_2\text{O}_2\text{CR}]_{10}\text{(hep)}_2] + 9\text{hepH} & \rightarrow \\
[\text{Fe}_6\text{O}_2\text{OH}](\text{O}_2\text{CR})_9(\text{hep})_4] & + \text{RCO}_2\text{H} + \text{H}_2\text{O} \\
\text{Fe}^{3+} & + 27\text{hep}^- + 6\text{hepH} + 63\text{H}_2\text{O}
\end{align*}
\]

In the case of benzoate complex 4, the crystal structure revealed a disorder at one of the bridging hep\(^-\) groups, whose site is still occupied by the \(\mu\)-OH\(^-\) group in 16\% of the molecules. This might indicate that the ligand substitution takes place in a sequential fashion, with a carboxylate group substituted first, followed by the hydroxide group.

The conversion of 1 and 2 to 3 and 4, respectively, is reversible. Recrystallization of 3 and 4 from hot acetonitrile gives 1 and 2, respectively. The conversion is sacrificial since no additional carboxylate was added, and the yields were accordingly not high.

An alternative route was found to 4 involving treatment of \([\text{Fe}_{11}\text{O}_6\text{OH}](\text{O}_2\text{CPh})_{15}\] with 11 equiv of hepH, which gave compound 4 in good yield (47\%), as summarized in eq 7.

\[
\begin{align*}
9[\text{Fe}_{11}\text{O}_6\text{OH}](\text{O}_2\text{CPh})_{15}] & + 99\text{hepH} \rightarrow \\
[\text{Fe}_{11}\text{O}_6\text{H}_2\text{O}](\text{O}_2\text{CPh})_9(\text{hep})_4] & + \\
9\text{Fe}^{3+} & + 27\text{hep}^- + 6\text{hepH} + 63\text{H}_2\text{O}
\end{align*}
\]

The reason for the formation of 4 instead of 2 probably lies in the lower availability of benzoate ligand, which is the limiting reagent in this reaction. The Fe\(_{11}\) starting material contains \(\sim 1.4\) benzoate groups per Fe, as opposed to the two per Fe in \([\text{Fe}_3\text{O}_2\text{CPh}](\text{H}_2\text{O})_3]^{10}\). In accord with this, the same reaction but also with 7 equiv of sodium benzoate per Fe\(_{11}\) (enough to give a total of two benzoates per Fe) now gave 2 instead of 4. However, when the reaction was carried out with benzoic acid instead of benzoate, the product was 4.

**Description of Structures.** \([\text{Fe}_6\text{O}_2\text{O}_2\text{CR}]_{10}\text{(hep)}_2] (1) and [\text{Fe}_6\text{O}_2\text{O}_2\text{OH}](\text{O}_2\text{CPh})_{10}(\text{hep})_2] (2).** Labeled ORTEP plots of \([\text{Fe}_6\text{O}_2\text{O}_2\text{CR}]_{10}\text{(hep)}_2] (2) from two viewpoints are presented in Figure 1; ORTEP plots of \([\text{Fe}_6\text{O}_2\text{O}_2\text{CPh}](\text{hep})_{10}] (1) are available elsewhere, and are very similar to those for 2. Selected bond distances and angles comparing 1 and 2 with 3 and 4 are listed in Table 2; the data for 1 are from this work for the nonsolvated, monoclinic form. Compounds 1 and 2 crystallize in monoclinic space groups and display crystallographic \(C_i\) symmetry; the asymmetric units therefore contain only half of an \(\text{Fe}_6\) molecule, and there are no solvent molecules in the cell. The structure comprises six Fe atoms in an almost planar arrangement that can be described as two triangular \([\text{Fe}_3(\mu_3-O)]\) units joined together at two of their apices. Each linkage comprises one bridging hydroxide and two bridging carboxylate groups, with the Fe–O(H)–Fe angle being 121.6(1)\(^\circ\) for 1 and 125.6(2)\(^\circ\) for 2. The \(\mu_3\)-oxide in each triangular unit is slightly out of the plane formed by the three Fe atoms (Fe1, Fe2, and Fe3) by 0.263 Å in 1 and 0.195 Å in 2. Each Fe\(_3\) triangle is scalene. In addition to the central \(\mu_3\)-oxide ion, Fe1 and Fe2 are bridged by two \(\mu_2\)-CR\(^-\) groups, whereas Fe1 and Fe3 are linked by one \(\mu_2\)-CR\(^-\) group and a \(\mu\)-alkoxo group from a hep\(^-\) ligand. Note that there are two monatomic bridges between Fe1 and Fe3, and this causes this Fe\(_{11}\)–Fe distance (2.9–3.0 Å) to be significantly shorter than the other two (3.2–3.3 and 3.5–3.6 Å). All the Fe atoms possess distorted octahedral coordination geometries. The overall structure is slightly distorted by the presence of intramolecular hydrogen bonds between the bridging hydroxido group and one of the oxygen atoms from the distal \(\text{O}_2\text{CPh}\) group. This is evidenced by the short separation of 2.926(2) Å between O2 and O11 in 2 (2.812(2) Å in 1).

For convenience in comparing the overall structures of 1 and 2 with 3 and 4, we will refer to the former as possessing a trans topology, referring to the relative disposition of the two short, monatomically bridged Fe\(_3\) pairs; as will be described below, 3 and 4 are then the cis isomer of this Fe\(_6\)
Structurally Related Fe₆ Molecular Clusters

Table 2. Principal Structural Parameters (Å, deg) for Complexes 1–4

<table>
<thead>
<tr>
<th>label</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tr>
<td>Fe−Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>3.570(2)</td>
<td>3.603(7)</td>
<td>3.5824(4), 3.5627(4)</td>
<td>3.587(6), 3.598(6)</td>
</tr>
<tr>
<td>C</td>
<td>2.933(2)</td>
<td>2.918 (7)</td>
<td>2.9185(4), 2.9390(4)</td>
<td>2.943(6), 2.935(7)</td>
</tr>
<tr>
<td>D</td>
<td>3.428(2)</td>
<td>3.488(7)</td>
<td>3.4423(4)</td>
<td>3.444(6)</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td>3.0753(4)</td>
<td>3.091(6)</td>
</tr>
</tbody>
</table>

| Fe−O  |     |     |     |     |
| a     | 1.900 (2) | 1.915(2) | 1.901(2), 1.880(1) | 1.905(2), 1.897(2) |
| b     | 1.884 (2) | 1.871(2) | 1.893(2), 1.882(2) | 1.883(2), 1.886(2) |
| c     | 1.961 (2) | 1.967(2) | 1.955(2), 1.936(2) | 1.964(2), 1.969(2) |
| d     | 1.972 (2) | 1.976(2) | 1.980(2), 2.000(2) | 1.982(2), 1.993(2) |
| e     | 2.001(2) | 1.998(2) | 1.990(2), 2.033(2) | 1.992(2), 1.993(2) |
| f     | 1.947(2), 1.979 (2) | 1.940(3), 1.981(3) | 1.951(2), 1.951(2) | 1.933(2), 1.948(2) |
| g     |     |     | 2.012(2), 2.020(2) | 2.031(2), 2.033(2) |
| h     |     |     | 1.967(2), 1.990(2) | 1.982(2), 1.974(2) |

| Fe−O−Fe |     |     |     |     |
| α     | 118.6(1) | 119.5(1) | 121.38(8), 120.38(8) | 120.3(1), 120.2(1) |
| β     | 136.4(1) | 139.6(1) | 137.16(8), 137.90(8) | 137.7(1), 137.9(1) |
| γ     | 98.9(1) | 97.5(1) | 98.39(7), 100.74(7) | 99.1(1), 98.74(9) |
| δ     | 95.2(1) | 94.5(1) | 93.56(7), 94.65(7) | 95.60(9), 94.88(8) |
| ε     | 121.6(1) | 125.6(2) | 124.07(8), 120.38(8) | 120.3(1), 120.2(1) |
| ξ     |     |     | 99.43(7) | 99.03(9) |
| θ     |     |     | 102.02(7) | 102.7(1) |

* Labels refer to those in Figure 2. † Crystallographic C₃ symmetry. ‡ Virtual C₃ symmetry; entries are grouped together under this symmetry.

Figure 2. Diagrammatic scheme of the core structures of complexes 1–4, and defining the distance and angle labels used in Table 2. Symmetry-equivalent quantities are not labeled.

µ-alkoxo group of a chelating hep⁻ ligand. There are again intramolecular hydrogen bonds across the central gap, this time between the oxygen atom of the bridging hydroxide group (O₃ in 3, O₂ in 4) and the oxygen atom of one of the alkoxide bridges (O₂ in both 3 and 4), with distances of 2.783(1) and 2.761(2) Å in 3 and 4, respectively.

It is interesting that the conversion of 1 and 2 to 3 and 4, respectively, by the incorporation of two extra hep⁻ groups, has not led to the latter being incorporated in a symmetric manner, but instead on the same side of the molecule.

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Nevertheless, this is likely the primary reason that the structures of 3 and 4 are distinctly different from those of 1 and 2 in a very important way: the two short, monatomically bridged Fe pairs (Fe2Fe3 and Fe4Fe5 for 3, and Fe1Fe3 and Fe4Fe6 for 4) are now on the same side of the molecule, and the core topology of 3 and 4 is thus described as cis. There are no previously reported examples of Fe6 compounds with this cis topology.

**Magnetism Studies. Compounds 1 and 2.** Variable-temperature, solid-state magnetic susceptibility measurements were performed on microcrystalline samples of 1 and 2 at 0.5 and 1.0 T, respectively, in the 2.0–300 K temperature range. The samples were restrained in eicosane to prevent torquing. The obtained data were very similar for both compounds and are shown in Figure 5 as effective magnetic moment ($\mu_{\text{eff}}$) per Fe6 versus $T$. The $\mu_{\text{eff}}$ at room temperature is 9.3 $\mu_B$, below the spin-only ($g = 2$) value expected for six noninteracting FeIII ions (14.49 $\mu_B$), indicating the presence of antiferromagnetic interactions. The $\mu_{\text{eff}}$ gradually increases with decreasing temperature, reaching a plateau of 10.8 $\mu_B$ at 20 K for 1 and 10.6 $\mu_B$ at 30 K for 2. These are very close to the spin-only value (10.95 $\mu_B$) calculated for a system with an $S = 5$ ground state. The $\mu_{\text{eff}}$ drops sharply at the lowest temperatures, reaching a minimum of...
average of the magnetization. The method is described in more detail elsewhere.\textsuperscript{20,21} The fits, shown as solid lines in Figure 6, gave $S = 5$, $g = 1.9550(5)$, $D = 0.458(3)$ cm$^{-1}$, and $E = \pm 0.046$ cm$^{-1}$ for complex 1, and $S = 5$, $g = 1.889(7)$, $D = 0.69(3)$ cm$^{-1}$, and $E \sim 0$ cm$^{-1}$ for compound 2. Alternative fits with different values of $S$ were discarded because they gave unreasonable values of $g$.

The $g$ versus $D$ error surfaces for the fits for compounds 1 and 2 were calculated to assess whether the values found for $g$ and $D$ do indeed correspond to the global rather than local minima. There are actually two minima in both cases, one with a positive $D$ value and the other with a negative one. This is as is typically found in such fits, which are not very sensitive to the sign of $D$. Nevertheless, the relative error of the fits for both compounds is smaller when $D > 0$. This fact, together with previously reported measurements of the magnetization relaxation behavior of 1 at very low temperatures,\textsuperscript{6} which is consistent with $D > 0$, supports the conclusion that compounds 1 and 2 have the $D$ values given above, both with $D > 0$.

Compounds 3 and 4. Variable-temperature, solid-state magnetic susceptibility measurements were performed on microcrystalline samples of 3 and 4 in a 1.0 T field in the 2.0–300 K temperature range. The samples were restrained in eicosane to prevent torquing. The data are plotted as $\mu_{\text{eff}}$ versus $T$ in Figure 7. The $\mu_{\text{eff}}$ steadily decreases from 8.5 $\mu_B$ for 3 and 8.8 $\mu_B$ for 4 at 300 K to 1.4 $\mu_B$ and 0.8 $\mu_B$ at 2.0 K for 3 and 4, respectively. As for 1 and 2, the values at 300 K are much lower than that expected for a cluster of six noninteracting Fe$^{II}$ ions with $g = 2$ (14.49 $\mu_B$), again indicating the presence of predominantly antiferromagnetic exchange interactions. In contrast to 1 and 2, however, the monotonically decreasing $\mu_{\text{eff}}$ with decreasing temperature and the resultant low value at 2.0 K are indicative of an $S = 0$ ground state for compounds 3 and 4.

The magnetic studies thus establish that the two groups of compounds, 1/2 and 3/4, have very different ground state spin values even though their structures are quite similar. This is a dramatic difference, corresponding to 10 unpaired electrons. The structures differ in only two significant ways: (i) the cis versus trans disposition of the two triangular Fe$^{III}$ units, and (ii) the change in the identity of two of the bridging ligands between the Fe$^{III}$ units. One or both of these differences could be the cause of the variation in $S$. Ultimately, the ground state spin must be dependent upon the various pairwise Fe$_2$ exchange interactions ($J$) in the molecule, since these will determine the alignment of the various spins in the molecule and thus its ground state $S$ value. But the pairwise Fe$_2$ exchange (actually superexchange) interactions are primarily determined by the bridging ligands across that Fe$^{III}$ pair and the attendant metric parameters, and these are all essentially the same in 1/2 and 3/4 except for the one difference noted as ii. Therefore, it could possibly be that a major change in the $J$ value at this

Figure 6. Plot of the reduced magnetization ($M/N_{\text{Av}}$) vs $HT$ for (top) complex 1 in applied fields of 1 ( ), 2 ( ), 3 ( ), 4 ( ), 5 ( ), 6 ( ), and 7 ( ) T, and (bottom) for complex 2 in applied fields of 1 ( ), 2 ( ), 3 ( ), 4 ( ), and 5 ( ) T. The solid lines are the fits of the data; see the text for the fitting parameters.

9.3 $\mu_B$ for 1 and 9.1 $\mu_B$ for 2 at 2.0 K, most likely due to zero-field splitting (ZFS) of the ground state, as well as weak intermolecular antiferromagnetic interactions.

In order to confirm the indication from the above data of an $S = 5$ ground state for 1 and 2, variable-temperature and -field magnetization ($M$) data were collected on the same samples of 1 and 2. Data were collected in the 1–7 T and 1.7–4.0 K field and temperature ranges. The obtained data are plotted as reduced magnetization ($M/N_{\text{Av}}$) versus $HT$, where $N$ is Avogadro’s number, in Figure 6. Both plots display nonsuperimposed isofield lines characteristic of a system with significant zero-field splitting (ZFS). The saturation values of the reduced magnetization at the highest fields and the lowest temperatures are around 9 $\mu_B$, slightly below the expected saturation value (10 $\mu_B$) for a ground state with $S = 5$ and $g = 2$. The data were least-squares fit by diagonalizing the spin Hamiltonian matrix, including axial ($D$) and rhombic ($E$) ZFS terms and Zeeman interactions, assuming that $g$ is isotropic and that only the ground state is populated at these temperatures, and calculating a full powder


computed for a set of UHF component wave functions using
in three stages. First, energies and spin couplings are
differences in either the couplings between Fe3 units (inter-
susceptible to spin frustration effects. In other words,
we carried out the calculations described below.

Assuming that the various exchange constants in the molecules. For this reason,
ecessary first step must be to obtain reliable values for the
observed difference. In any event, it is clear that if the large
spin differences are to be explained in a quantitative manner
rather than merely being qualitatively assigned as somehow
due to the two identified structural differences, then a
ecessary first step must be to obtain reliable values for the
various exchange constants in the molecules. For this reason,
we carried out the calculations described below.

**Semiempirical Calculations.** Semiempirical calculations
using the ZILSH method were performed to analyze the
exchange interactions underlying the magnetic properties
observed for complexes 1–4. These calculations take place
in three stages. First, energies and spin couplings are
computed for a set of UHF component wave functions using
the INDO/S model of Zerner. Estimates of the exchange
constants (J) are then obtained from these quantities by
simultaneous solution of eqs 2. In the second stage, the
exchange constants are adjusted using the genetic algorithm
fitting method to more closely reproduce the experimentally
measured variable-temperature magnetic susceptibility of the
complexes. In the third and final stage, the exchange
constants found in the second stage are substituted into the
Heisenberg spin Hamiltonian, which is diagonalized in a
basis of spin components (eq 4) to yield the final energies
and wave functions of the spin states. Results for each stage
of the calculations are discussed in turn below.

The exchange constants found for complexes 1–4 from
the energies and spin couplings of UHF component wave
functions are given in Table 3. All interactions are antifer-
romagnetic, as expected for high-spin Fe3+ (d^5) ions. The
values obtained reflect the symmetry of the complexes; 1
and 2 have crystallographic inversion symmetry, so four
unique exchange constants (J_A, J_B, J_C, and J_D for interactions
A, B, C, and D in Figure 2) were obtained for these
complexes. In contrast, 3 and 4 have lower crystallographic
symmetry, resulting in distinct values for all eight nonzero
exchange constants. There is, however, a virtual plane of
symmetry relating the two triangular subunits, as can be seen
by comparing J_A and J_A’ (e.g., −42.5 vs −44.6 cm\(^{-1}\)) in
complex 3). J_C and J_C’ (−20.1 and −24.0 cm\(^{-1}\)), and J_B and
J_B’ (−47.9 and −53.4 cm\(^{-1}\)). All exchange constants other
than those given in Table 3 (and their symmetry-equivalent
partners) were found to be zero. The nonzero values obtained
for each interaction are similar in all four complexes, which
is not surprising given their similar structures and ligands.

It is important to consider the spin couplings computed
from the UHF wave functions in evaluating how accurate

![Figure 7. Plot of the effective magnetic moment per Fe6 vs temperature for [Fe_3O_7(OH)(O_2CCH_3)_6] (top) and [Fe_3O_7(OH)(O_2CPh)_6] (bottom). The solid line corresponds to the theoretical fit (see the text for details).](image-url)
the predicted exchange constants are. Values of the local spin moments \(\langle S_A^z \rangle\) and spin couplings \(\langle S_A^z S_B^z \rangle\) for single determinant approximations of the ground-state wave functions of complexes 1–4 are given in Table 3. As stated earlier, exchange constants extracted from single determinant wave functions are formally equal to those of the spin states of the system if the determinant wave functions are high spin eigenfunctions of the local spin operators \(S_A^z\). If that were the case, values of \(S_A(S_A + 1) = 8.75\) would be obtained for high spin Fe\(^{3+}\) ions, which have spin quantum numbers of \(\tfrac{5}{2}\). The values given in Table 3 are reasonably close to this for all four complexes. Another measure of how closely the exchange constants resemble those of the spin states is given by the expectation value of the total spin operator, \(\langle S^z \rangle\). If the determinants were high-spin eigenfunctions of the local spin operators, this expectation value would be given by eq 3. Values found for the components described in Table 3 are similar to the values of 40 and 15 predicted by the equation.

One interesting contrast in Table 3 is that the expectation values of the total spin operator obtained for the complexes with PhCO\(_2^-\) ligands (2 and 4) are significantly further from the values given by eq 3 than are those for the complexes with Bu'CO\(_2^-\) ligands (1 and 3). Although we have not examined this in detail, it appears that this discrepancy arises from differences in local spin expectation values for the carbon atoms on the substituent groups, rather than from any differences in local spins or spin couplings of the metal ions. This is supported by the results of Table 3, in which the local spins and spin couplings involving the metal ions are similar for all four complexes.

The results of the previous paragraph demonstrate that the error caused by using UHF components that are not formally high-spin eigenfunctions of local spin is reasonably small. It is important to note that the local spin expectation values in Table 3 are very similar for the \(S = 0\) and \(S = 5\) complexes. This indicates that the exchange constants found for all complexes should be of comparable accuracy despite the difference in spin. This is not generally true for spin-dependent quantities obtained from single determinant wave functions due to the so-called “spin contamination”. It occurs in this case because spin contamination errors in the energies are exactly compensated for by spin contamination errors in the local spin couplings \(\langle S_A^z S_B^z \rangle\). In other words, both the energy on the left side of eq 2 and the spin coupling on the right side of eq 2 are contaminated by a linear combination of higher spin states, with the same expansion coefficients on both sides. These then cancel, yielding uncontaminated values for the exchange constants. This is formally demonstrated, and thoroughly discussed, in ref 7.

There is some error inherent in the parametrization of the INDO/S method that would be present even if a basis of local spin eigenfunctions were used to obtain the exchange constants. In our previous experience,\(^{7,11}\) exchange constants obtained from ZILSH provide a qualitatively correct description of exchange interactions in a complex, and correctly predict the ground state spin in most cases. However, ZILSH exchange constants typically do not closely reproduce experimental magnetic susceptibility data in a quantitative sense. This was the case for the complexes considered here, so the ZILSH/genetic algorithm method was used to further refine the results.

The exchange constants calculated by ZILSH served as a valuable starting point for the susceptibility fits and provided reasonable models for fitting, with the constants that were found to be equivalent being set equal in the fits. Thus, four unique, nonzero exchange constants were allowed to vary in the fits for complexes 1 and 2 \((J_{12} = J_{56}, J_{13} = J_{56}, J_{23} = J_{45},\) and \(J_{24} = J_{35};\) see Figure 8 for the numbering scheme), along with the \(g\) factor and the temperature independent paramagnetism (TIP). In complexes 3 and 4, five independent values were used in the fits \((J_{12} = J_{46}, J_{13} = J_{56}, J_{23} = J_{45}, J_{24},\) and \(J_{35}\)) along with the \(g\) factor and the TIP. All parameters \((J’s, g,\) and TIP) were varied simultaneously to minimize the difference between calculated and experimental magnetic susceptibility at each temperature. The resulting exchange constants are given in Table 4, and the predicted magnetic susceptibilities are shown as the solid lines in Figure 5 (for 1 and 2) and Figure 7 (for 3 and 4).

The exchange constants obtained for complexes 1 and 2 agree well with values found by a fit for the analogous \((S = 5)\) complex \([Fe_6O_2(OH)_2(O_2CCH_3)_{10}L_2]^{18,19,22}\) with a trans topology, where L is an imidazole-based ligand with formula \(C_6H_4\)N\(_2\)O\(^-\). In that work, values of \(-38\) cm\(^{-1}\) were found

for $J_{12}$ and $J_{23}$ (these parameters were artificially made equivalent in ref 23), $-6$ cm$^{-1}$ for $J_{13}$, and $-8$ cm$^{-1}$ for $J_{34}$, comparable to those found for 1 and 2 (Table 4). The exchange constants obtained for 3 and 4 are also rather similar to those found for 1 and 2. This is as expected, because the corresponding pairwise Fe$_2$ exchange interactions have similar bridging ligands and bridging geometries. Also, the $g$ factors given in Table 4 for 1 and 2 agree well with the values obtained by fitting the magnetization versus field data given above, 1.975 versus 1.955, and 1.939 versus 1.889, respectively.

Substitution of the exchange constants of Table 4 into the Heisenberg spin Hamiltonian (HSH) and diagonalization provide predictions for the ground state spins of the complexes. Compounds 1 and 2 are calculated to have ground state spins of $S = 5$, and 3 and 4 to have ground states of $S = 0$, in perfect agreement with the experimental data discussed in the previous section. The ground-state wave functions obtained for 1 and 2 are described in Table 5. They are dominated by a single component, |$\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\rangle$, where the arrows indicate $M_A = \pm 7/2$, using the numbering scheme of Figure 8. In both complexes, this component comprises almost half of the ground state wave function. The expectation values of $M_A$ found in these ground states reflect the same alignment of spins, but with magnitudes reduced from $\pm 7/2$ by the admixture of other components into the wave function. In these complexes with $S = 5$ ground states, both the leading contributions to the wave function and the local $z$-components provide a clear picture of the spin alignments in the ground state.

In contrast, for 3 and 4 the leading contributions are made by components representing less than 12% of the wave function, and the local $z$-components of spin $M_A$ are zero.

This is typical for singlet states. In these cases, the average spin couplings $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ computed from the spin state wave function give a better indication of the spin alignments. Positive values of $\langle \hat{S}_A \cdot \hat{S}_B \rangle$ indicate parallel alignment, whereas negative values indicate antiparallel alignment. These expectation values are given for all nonzero interactions in the ground states of the four complexes in Table 6. They show that the spins of Fe$_1$ and Fe$_3$ are aligned parallel in all four complexes. The spins of Fe$_4$ and Fe$_5$ are aligned parallel in complexes 1 and 2, while the spins of Fe$_3$ and Fe$_6$ are aligned parallel in complexes 3 and 4. As discussed in the next section, this difference determines the spin of the ground state of each complex.

**Spin Frustration and the Ground State Spins of Complexes 1–4.** The pairwise Fe$_2$ exchange constants given in Table 4 for complexes 1–4 show that all nonzero interactions in these complexes are antiferromagnetic. Each pair of interacting spins would thus align antiparallel in the absence of other interactions. Nevertheless, as can be seen in Figure 8, two pairs of interacting spins are aligned parallel in each complex in the ground state. The reason for this is spin frustration. Spin frustration can be defined in a general sense as the presence of competing antiferromagnetic exchange interactions. When these are all of comparable strength, a balance is reached, and the ground state spin alignments become very sensitive to the relative magnitudes of the competing interactions. In contrast, when the competing interactions are of significantly different strengths, then the strongest ones prevail and align the spins they control antiparallel, whereas the weakest ones are totally frustrated.

This leads to the situation where the interaction between a pair of metals may be antiferromagnetic but the spins on these metals will nevertheless be aligned parallel due to the influence of stronger exchange interactions in adjacent metal pairs. Such effects are commonly encountered in a triangular arrangement of three antiferromagnetically coupled metal ions. In this topology, it is impossible for each of the spins to be aligned antiparallel to both of its neighbors.

Complexes 1–4 contain an Fe$_6$ topology that comprises two Fe$_3$ triangular units, and because the calculations described have determined that all the interactions are antiferromagnetic, spin frustration effects can be expected. Indeed, spin frustration has previously been invoked to explain the magnetic properties of other Fe$_6$ compounds with the trans topology of 1 and 2 and a resulting $S = 5$ ground state. In the discussion below, we show that the results of our calculations confirm how the $S = 5$ ground state arises for the trans topology, but more importantly, it also becomes clear why the newly discovered cis topology of 3 and 4 naturally leads to an $S = 0$ ground state. As will be seen, the answer lies in the differing relative distribution of totally frustrated exchange pathways in the cis versus trans forms.

The significant difference in strength between exchange constants in 1–4 leads to some interactions being totally frustrated. The distribution of frustrated pathways and the resulting spin alignments are shown in Figure 8, where the frustrated pathways are denoted by dashed lines. The

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frustrated interactions are, of course, those with the weakest exchange constants, and they are overlapped by the other, stronger interactions. Although all interactions are antiferromagnetic in these Fe3⁺ complexes, the frustrated pathways are readily identified as those with positive average spin couplings (Table 6): Thus, the Fe1–Fe3 and Fe4–Fe6 pathways are frustrated in complexes 1 and 2, and the Fe1–Fe3 and Fe5–Fe6 pathways are frustrated in 3 and 4.

Now it can easily be seen that the trans and cis topologies will lead to S = 5 and S = 0 ground states for 1/2 and 3/4, respectively, because they will determine the relative disposition of the frustrated pathways. In 1 and 2, the frustrated pathways are Fe1/Fe3 and Fe4/Fe6 (Figure 5A), which are disposed trans in the molecule and thus are separated by Fe2 and Fe5, with which they couple antiferromagnetically and thus align their spins antiparallel. But as a result, the two separate pairs of parallel-aligned spins in the frustrated pathways are mutually parallel, and the trans molecule’s total spin is therefore S = 10 = 5. In contrast, the frustrated pathways in 3 and 4 are Fe1/Fe3 and Fe5/Fe6 (Figure 5B), and they are adjacent. As a result, the spins of Fe3 and Fe5 directly couple and align antiparallel, and the two pairs of parallel-aligned spins in the frustrated pathways are consequently mutually antiparallel. Since the spins Fe2 and Fe4 are also aligned antiparallel, the cis molecule’s total spin is S = 15/2 – 15/2 = 0. Thus, the calculated ground state S is directly determined by the trans (S = 5) or cis (S = 0) relative disposition of the two frustrated pairs, in perfect agreement with the experimental measurements described above.

The alternative hypothesis to explain the difference in ground state spins of the cis and trans forms given above was that variations in the couplings between the two triangular Fe₃O units (interunit couplings) lead to the spin reversal. In such a model, each Fe₃O unit would be considered to have a total spin of 5/2, and these spins would then couple to give states with total spins ranging from 0 to 5. Variations in the interunit couplings could then lead to the observed reversal of spin. While there is considerable variation in the exchange constants found for the interunit pathways in the four complexes (Table 6), two important points make this alternative explanation unlikely. First, the ground state spins in complexes 1–4 do not change when the exchange constants for the interunit pathways are allowed to vary over wide ranges of values. For complex 1, for example, the interunit pathways both have J = –17.0 cm⁻¹ in the ground state. Even if these values are reduced to J = –0.05 cm⁻¹ or increased to –100 cm⁻¹, the ground state still has S = 5. A similar result holds for complexes 3 and 4 with singlet ground states: as long as the interunit couplings are antiferromagnetic, singlet ground states are obtained regardless of the magnitude of the interunit exchange constants. It is thus unlikely that variations in the values of these exchange constants between the various complexes could lead to the spin reversal.

The second point in favor of the cis–trans hypothesis is based on similar reasoning involving the couplings within the triangular Fe₃O units. It is quite easy to demonstrate that the spin reversal occurs as the frustrated pathways change from cis to trans, by allowing the exchange constants in one

### Table 4. Exchange Constants for 1–4 Obtained Using the Genetic Algorithm Method

<table>
<thead>
<tr>
<th>parameter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>J₁₂</td>
<td>–34.0 (–40.3)</td>
<td>–29.9 (–39.0)</td>
<td>–30.8 (–42.5, –44.6)</td>
<td>–27.2 (–40.9, –42.8)</td>
</tr>
<tr>
<td>J₁₃</td>
<td>–7.5 (–21.4)</td>
<td>–3.5 (–15.9)</td>
<td>–16.1 (–20.1, –24.0)</td>
<td>–7.7 (–20.3, –22.1)</td>
</tr>
<tr>
<td>J₂₃</td>
<td>–46.9 (–50.8)</td>
<td>–39.1 (–55.6)</td>
<td>–32.9 (–47.9, –53.4)</td>
<td>–38.1 (–48.0, –49.0)</td>
</tr>
<tr>
<td>J₃₄</td>
<td>–17.0 (–24.2)</td>
<td>–17.4 (–28.5)</td>
<td>–21.0 (–29.1)</td>
<td>–35.1 (–31.3)</td>
</tr>
<tr>
<td>J₅₆</td>
<td>–7.5 (–24.0)</td>
<td>–7.5 (–24.0)</td>
<td>–7.5 (–24.0)</td>
<td>–4.1 (–20.1)</td>
</tr>
<tr>
<td>g</td>
<td>1.975</td>
<td>1.939</td>
<td>1.996</td>
<td>1.900</td>
</tr>
<tr>
<td>TIP</td>
<td>1.165 × 10⁻⁶</td>
<td>982 × 10⁻⁶</td>
<td>1.134 × 10⁻⁶</td>
<td>915 × 10⁻⁶</td>
</tr>
<tr>
<td>σ⁴</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a Numbering scheme as in Figure 8; the numbers in parentheses are those obtained from the ZILSH calculation (Table 3). b Parameters assumed to be symmetry-equivalent are not included. c J values in cm⁻¹. TIP in cm³ mol⁻¹. d Sum of differences between experimental and calculated values of χₐT over all temperatures.

### Table 5. Ground State Properties of 1–4 Computed with the Heisenberg Spin Hamiltonian

<table>
<thead>
<tr>
<th>compd</th>
<th>S (weight)</th>
<th>leading contribution</th>
<th>2S, (Fe₁)</th>
<th>2S, (Fe₂)</th>
<th>2S, (Fe₃)</th>
<th>2S, (Fe₄)</th>
<th>2S, (Fe₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>[[H] H] (0.439)</td>
<td>4.63</td>
<td>–3.98</td>
<td>4.35</td>
<td>4.35</td>
<td>–3.98</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>[[H] H] (0.452)</td>
<td>4.63</td>
<td>–4.01</td>
<td>4.39</td>
<td>4.39</td>
<td>–4.01</td>
</tr>
</tbody>
</table>

a Numbering scheme as in Figure 8. b Exchange constants listed in Table 4 were used in all cases. c Format [[123456]].

### Table 6. Exchange Constants (J), Average Spin Couplings (〈SᵢSⱼ〉), and Contributions to the Total Energy (ΔE) for the Ground States of 1–4

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>〈SₓSᵧ〉</td>
<td>ΔE</td>
<td>〈SₓSᵧ〉</td>
<td>ΔE</td>
</tr>
<tr>
<td>Fe₁–Fe₂</td>
<td>−34.0</td>
<td>−7.13</td>
<td>−484.8</td>
<td>−29.9</td>
</tr>
<tr>
<td>Fe₁–Fe₃</td>
<td>−7.5</td>
<td>6.16</td>
<td>92.4</td>
<td>−3.5</td>
</tr>
<tr>
<td>Fe₁–Fe₄</td>
<td>−46.9</td>
<td>−7.47</td>
<td>−700.7</td>
<td>−39.1</td>
</tr>
<tr>
<td>Fe₁–Fe₅</td>
<td>−17.0</td>
<td>−6.17</td>
<td>−209.8</td>
<td>−17.4</td>
</tr>
<tr>
<td>Fe₁–Fe₆</td>
<td>−7.5</td>
<td>−7.57</td>
<td>−113.6</td>
<td>−7.5</td>
</tr>
</tbody>
</table>

a ΔE = −2Jₐₖ(〈SₓSⱼ〉). Numbering scheme as in Figure 8. b cm⁻¹. c cm⁻¹.
Fe₃O unit to vary. For complex 1, the frustrated pathways $J_{13}$ and $J_{46}$ (−7.5 cm⁻¹; see Figure 8 for numbering scheme) are in the *trans* relationship, as are the more strongly coupled pathways $J_{12}$ and $J_{56}$ (−34 cm⁻¹). The ground-state spin is then $S = 5$. If, hypothetically, these values were switched on one side of the complex ($J_{46}$ was −34 cm⁻¹ and $J_{56}$ was −7.5 cm⁻¹), then the frustrated pathways would be in the *cis* relationship. These switched values lead to a ground state spin of $S = 0$.

A plot of the energies of the $S = 5$ and $S = 0$ states versus $J_{46}$ and $J_{56}$ for complex 1 (Figure 9) clearly shows how the ground state spin changes as the frustrated pathways switch from *trans* to *cis*. At the left side of the plot, $J_{46} = −7.5$ cm⁻¹ and $J_{56} = −34$ cm⁻¹, the frustrated pathways are *trans*, and the ground state is $S = 5$ by a considerable margin. At the right side of the plot, $J_{46} = −34$ cm⁻¹, $J_{56} = −7.5$ cm⁻¹, the frustrated pathways are *cis*, and the ground state is $S = 0$. The cartoons at each side of the figure illustrate these extremes by showing the frustrated pathways as dashed lines. Moving from left to right on the plot, the spin reversal occurs as $J_{46}$ becomes larger than $J_{56}$, and the pathway that is frustrated in the ground state goes from $J_{46}$ to $J_{56}$. (Between the two extremes, the identities of the $S = 0$ and $S = 5$ states were established by monitoring the values of $\langle \hat{S}_A \hat{S}_B \rangle$ for different values of $J_{46}$ and $J_{56}$. In particular, these quantities conclusively indicate which pathway is frustrated.) This convincingly demonstrates that the spin reversal is indeed occurring because of the arrangement of frustrated pathways, either *cis* or *trans*.

As mentioned earlier, the spin coupling value $\langle \hat{S}_A \hat{S}_B \rangle$ is useful for analyzing spin frustration effects because it represents the actual alignment of the spins of metal centers A and B in the spin state. It is positive and negative for parallel and antiparallel alignments, respectively. The $J$ values merely reflects the preferred alignment. If $\langle \hat{S}_A \hat{S}_B \rangle$ and $J_{AB}$ differ in sign, the A–B pathway is frustrated. In a more quantitative sense, the product $−2J_{AB}\langle \hat{S}_A \hat{S}_B \rangle$ (referred to as $\Delta E$ in Table 6) represents the contribution made by the A–B pathway to the total energy of the spin state (see eq 2). The interaction of spins through frustrated pathways thus increases the total energy of the system. With this definition, it is clear why complete spin frustration occurs in pathways with the weakest exchange constants: the energy is increased only slightly by the frustrated interaction, which is more than compensated for by larger increases in the energy in other pathways with stronger exchange constants. This is demonstrated by the values of $\Delta E$ in Table 6, where the positive contributions from the frustrated pathways are much smaller than the negative contributions from other pathways.

The quantity $\Delta E$ provides a quantitative measure of which pathways stabilize the $S = 5$ state below the $S = 0$ state in complexes 1 and 2, and vice versa for complexes 3 and 4. In complex 1, for example, the values of $\Delta E$ given in Table 6 for the $S = 5$ ground state indicate a total energy of −2606 cm⁻¹ for this state (considering all symmetry-equivalent pathways). Of this total, −2186 cm⁻¹ is contributed by the intraunit pathways (those within Fe₃O subunits, i.e., $1−2, 1−3, 2−3, 4−5, 4−6, \text{ and } 5−6$ in Figure 8), while −420 cm⁻¹ is contributed by the interunit pathways (2−4 and 3−5).

Table 7 lists the energies of the $S = 5$ and $S = 0$ states of complexes 1 (ground state $S = 5$) and 3 (ground state $S = 0$), along with contributions from the interunit and intraunit pathways. For complex 1, it can be seen by subtracting the energies in Table 7 that the $S = 5$ state is stabilized relative to the $S = 0$ state by 461 cm⁻¹ (given as $E_{S=5} - E_{S=0}$ in the table). Similarly, it can be seen that the intraunit pathways contribute 374 cm⁻¹ to this stabilization (given as $\Delta(\Delta E)$, intraunit pathways in Table 7), while the interunit pathways contribute only 87 cm⁻¹.

Turning now to complex 3, in this case the $S = 0$ state is the ground state, and is stabilized relative to the $S = 5$ state by 240 cm⁻¹. The intraunit pathways contribute 182 cm⁻¹ to this total, while the interunit pathways contribute only 58 cm⁻¹. In both cases, it is apparent that while the interunit pathways do make small contributions to the stabilization energy, the primary contributions are made by the intraunit pathways. Since the only topological difference between the intraunit couplings in the $S = 5$ and $S = 0$ complexes is the topology of frustrated pathways, either *cis* or *trans*, this must then be the primary factor determining which state is more stable.

**Magnetostructural Relationships.** The above discussion has successfully rationalized the variation of the spins of the *trans* and *cis* Fe₆ core “isomers” based on the exchange constants. It is also important to consider the relationship between them and the structural parameters that determine their magnitude. Such a correlation would be useful for rationalizing observed magnetic properties of polynuclear complexes, and it could also assist in the deliberate synthesis of complexes with desirable magnetic properties (e.g., large spin ground states). Most attempts to date to establish magnetostructural correlations have focused on dinuclear systems, including hydroxide-bridged dicopper(II)²⁴ and dichromium(III)²⁵ complexes, oxide-bridged dimanganese(IV) complexes,²⁶ phenoxy-bridged dinickel(II) complexes,²⁷ and


Structurally Related Fe\textsubscript{6} Molecular Clusters

oxide- hydroxide-, and alkoxide-bridged diiron(III) complexes.\textsuperscript{28-34} In all cases, empirical or semiempirical relationships have been established between the exchange constant and the M–O–M angles or M–O bond lengths in the bridges.

Focusing now on the diferric complexes, Gorun and Lippard reported an exponential relationship between the exchange constant and a parameter related to Fe–O distances in oxide-bridged complexes.\textsuperscript{28} The Fe–O–Fe angle was found to have only a second-order effect, a conclusion supported by ab initio calculations on Cl\textsubscript{3}Fe–O–FeCl\textsubscript{3}.\textsuperscript{29} Weihe and Güdel\textsuperscript{30} used a formulation based on the angular overlap model (AOM) to derive an expression for $J$ as a function of both the Fe–O–Fe angle ($\phi$) and the Fe–O distance ($r$) (eq 8).

$$J = A(B + C \cos \phi + \cos^2 \phi) \exp(Dr) \quad (8)$$

A fit to experimental data for a number of oxide-bridged diiron(III) complexes indicated that the magnetic interaction decreases when the Fe–O distance increases or when the Fe–O–Fe angle increases. Other, less extensive studies have also shown some dependence on angle.\textsuperscript{31-33} More recently, Werner et al. studied the previously reported correlations in an extensive group of hydroxide-, alkoxide-, and phenoxide-bridged iron (III) dimers.\textsuperscript{34} They applied both the exponential model of Gorun and Lippard\textsuperscript{28} and eq 8. These authors concluded that angular dependence is small.

Despite the extensive literature devoted to magnetostuctural correlations in dinuclear iron(III) compounds, very little has been reported on polynuclear complexes. The four Fe\textsubscript{6} compounds presented in this work provide sufficient independent exchange constants to allow a statistically meaningful magnetostuctural correlation to be obtained for diferric units within polynuclear topologies. Tables 2 and 4 list the relevant structural and magnetic data. In a first attempt to correlate the magnetic and structural parameters, we employed an exponential expression similar to that of Gorun and Lippard.\textsuperscript{28} The regression error obtained for a fit of the data using this expression was extremely large ($r = 0.70$). A closer examination of the parameters in Table 2, however, reveals a distinct relationship between the Fe–O–Fe angle and the coupling constant, in contrast to what was observed for dinuclear complexes. This is clearly displayed by Figure 10. In view of this, we next considered eq 8 as a model that includes both a radial and angular dependence.

The parameters of eq 8 that yield the minimum least-squares error are $A = 2 \times 10^7$ cm$^{-1}$, $B = 0.2$, $C = -1$, and $D = -7$ Å$^{-1}$. Whenever more than one bridge was present, the best results were obtained by employing the average distance for the shortest Fe–O bridge, which in all cases corresponds also to the one with a widest Fe–O–Fe angle. The results of the fit are shown in Figures 11 and 12. Figure 11 shows the three-dimensional surface representing the $J$ values for every combination of Fe–O–Fe angle ($\phi$) and Fe–O distance ($r$) as predicted from the correlation, together with the experimental values. A plot comparing the predicted and experimental $J$ values of 1–4 is presented in Figure 12.

The quality of the fit is very high, with a regression coefficient ($r$) of 0.94, whereas the same parameter for Weihe and Güdel’s results for dinuclear complexes was 0.82.\textsuperscript{30}

The picture that emerges for these hexanuclear complexes is that there is clearly both a radial and an angular dependence of the exchange constant. The exchange becomes more strongly antiferromagnetic (i.e., $J$ has a larger negative value) as the Fe–O distance decreases and as the Fe–O–Fe angle decreases.
polynuclear compounds, the situation is much more complex. In the case of so that no significant net angular dependence is observed; angle changes, these dependencies compensate each other interactions with different angular dependencies. When the dinuclear complex uses different d-orbitals to establish eliminates any angular dependence. Every Fe$^{3+}$ constant points (which is a two-dimensional projection of the surface in Figure 11 showing the iso-J curves (curves with the same value of exchange coupling constant J) for different combinations of Fe–O–Fe angle ($\varphi$) and average Fe–O distance (r)). Fe angle increases. This behavior is illustrated in Figure 13, which is a two-dimensional projection of the surface in Figure 11 showing the iso-J lines (lines of constant value of J) as a function of r and $\varphi$. It can be seen that the angular dependence is accentuated as r decreases, and the radial dependence is more important at wider angles. While the observation of a radial dependence was expected and is in accord with previous studies on dinuclear iron(III) compounds, the strong angular dependence is surprising and unprecedented.

The relative insensitivity of J to the Fe–O–Fe bridging angle in dinuclear compounds is thought to arise from the isotropic d-electron distribution of a high spin d$^5$ ion, which eliminates any angular dependence. Every Fe$^{3+}$ ion in a dinuclear complex uses different d-orbitals to establish interactions with different angular dependencies. When the angle changes, these dependencies compensate each other so that no significant net angular dependence is observed; any decrease in overlap involving one 3d orbital is compensated by increases involving other 3d orbitals. In the case of polynuclear compounds, the situation is much more complex.

Every metal center and its orbitals are involved in interactions with more than one other ion, and this will likely prevent the kind of compensation mentioned above and thus allow an angular dependence of J to be manifested. It is worth noting that our results agree with the predictions of Gerloch et al. They showed that all possible exchange interactions between two iron(III) ions would lead to antiferromagnetism except for a ferromagnetic contribution that arises from an exchange interaction through two orthogonal orbitals in the bridging atom. This ferromagnetic contribution is operative when the angle approaches 90° and could be contributing to the results we observe.

**Conclusions**

Treatment of the trinuclear compounds [Fe$_3$O(O$_2$CR)$_6$ (hep)$_3$]$^{0+}$ (R = Bu$, \text{Ph}$) with 3 equiv of hepH represents a convenient route to the hexanuclear compounds [Fe$_6$O$_2$(OH)$_2$ (O$_2$CR)$_9$(hep)$_2$] (R = Bu (1), Ph(2)) with a previously observed trans topology. The reaction of preformed 1 and 2 with an excess of hepH yields the structurally related hexanuclear compounds [Fe$_6$O$_2$(OH)(O$_2$CR)$_8$(hep)$_2$] (R = Bu (3), Ph(4)), with an unprecedented cis topology. This transformation can be reversed by recrystallization from acetonitrile. Both types of complexes contain two triangular [Fe$_3$(t$_2$-O)(O$_2$CPh)$_3$(hep)]$^{3+}$ units connected at two of their apices. However, 1 and 2 differ slightly from 3 and 4 in the means by which the two Fe$_3$ units are linked together, in either a trans or cis arrangement, which results in dramatically different magnetic properties. Magnetic data show 1 and 2 to have an S = 5 ground state and positive zero-field splitting, whereas 3 and 4 are diamagnetic. This large variation of 10 unpaired electrons in the net S values stresses the sensitivity of the magnetic properties of these polynuclear species to relatively small structural variations.

The semiempirical molecular orbital method ZILSH has proven a particularly useful way to explain the differences observed. It has allowed good estimates of the exchange constants of each complex to be obtained, which can then be refined by a genetic algorithm fit to the experimental variable-temperature magnetic susceptibility data. It has allowed also the spin topology of the ground states to be determined. As a result, it has been established that the large difference of 10 unpaired electrons in the net spin of the ground states is the direct consequence of a single structural difference between the two types of complexes, the relative disposition of the two completely frustrated exchange pathways whose spins are forced to align parallel by other, stronger interactions. It is thus now perfectly clear why the trans and cis Fe$_3$ topological isomers lead to S = 5 and S = 0 ground states, respectively. It is worth emphasizing that the change in one of the bridging sets linking the two Fe$_3$ subunits within the Fe$_6$ structure, from [($\mu$-OH)($\mu$-O$_2$CR)$_2$] in 1 and 2 (e.g., between Fe3 and Fe2’ in Figure 1) to [($\mu$-OR)$_2$($\mu$-O2CR)] in 3 and 4 (e.g., between Fe3 and Fe4 in Figure 3, top), does significantly change the J value within this Fe$_2$ pair, but that the latter per se is not the cause of the change in ground state S. In both cases, the J value at this position is negative (antiferromagnetic); this exchange.
interaction is not competing with any other to align spins, and thus, the magnitude of $J$ at this position is irrelevant to the spin frustration effects that determine the ground state. Nevertheless, this change in bridging ligands is indirectly crucial to the change in $S$ because it very much appears that it causes the structural change from trans to cis topology that then does affect the ground state spin value.

Finally, a magnetostructural correlation has been established that relates the exchange interaction constants $J$ with both the average Fe–O distance and the Fe–O–Fe angle through the shortest Fe–O–Fe bridge. In effect, this correlation is for Fe$_2$ pairs whose Fe atoms are also involved in additional bridging interactions with other Fe atoms. The correlation indicates that the antiferromagnetic interaction is stronger as the Fe–O–Fe angle increases and the Fe–O distance decreases, which is qualitatively logical. Despite the complexity of the Fe$_6$ molecules considered, the variation of the exchange constants can be correlated to only one of the exchange pathways between each pair of related ions, the one with the larger angle and shortest length. Moreover, the identity of the bridge (O$_2^-$, HO$^-$, or RO$^-$) does not itself affect the interaction, other than its influence on the corresponding bond distances and angles. We feel this correlation should prove useful in the future, both for hindsight rationalization of experimentally determined ground states, and for prediction of the exchange constants and ground states of new polynuclear complexes. The latter could also be particularly useful for predicting the position of the weakest interactions, which are likely to be totally frustrated, and thus predicting how the ground state would vary with isomeric changes in the Fe$_x$ topology, as we did in the present work for $1$–$4$. This is one of the most difficult questions to answer in polynuclear complexes, and yet extremely important especially in the directed design of species with desirable magnetic properties.

Acknowledgment. This work was supported by the National Science Foundation.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes [Fe$_6$O$_2$(OH)$_2$(O$_2$CBu')$_{10}$(hep)$_2$] (1), [Fe$_6$O$_2$(OH)$_2$(O$_2$CPh)$_{10}$(hep)$_2$] (2), [Fe$_6$O$_2$(OH)(O$_2$CBu')$_9$(hep)$_4$] (3), and [Fe$_6$O$_2$(OH)(O$_2$CPh)$_9$(hep)$_4$]·3MeCN (4·3 MeCN). This material is available free of charge via the Internet at http://pubs.acs.org.