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Magnetostructural Correlations in Polynuclear Complexes: The Fe_4 Butterflies

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Abstract: Theoretical methods based on density functional theory have been employed to analyze the exchange interactions in Fe_4 butterfly complexes. Three exchange coupling constants, calculated using a hybrid functional, provide an accurate description of the experimental magnetic susceptibility. The largest coupling constant corresponds to the interaction between the central and external iron atoms and presents a strong dependence on the Fe−O bond distance and the Fe−O−Fe angle of the central Fe_2O_2 core. An excellent linear correlation is found between such exchange coupling constants and a function of the spin population of the iron atoms, that is related with the square of the overlap of the “magnetic orbitals”, according to the Kahn−Briat model.

Introduction

The research in molecular magnetism has pursued during the last years polynuclear transition metal complexes that present a slow relaxation of their magnetization at low temperature, the so-called single-molecule magnets (SMM).[1] The requirements for such systems to have a high barrier are a large ground state spin and a large negative magnetic anisotropy. A variety of single-molecule magnets containing several transition metal atoms have been characterized to date: among them the most widely studied complexes are the Mn_{12} and Fe_8 systems, both with $S = 10$.[2,3] The sign and the strength of the exchange interactions that are a physical characteristic of the system[4−7] will control the value of the ground state spin. Hence, there is a clear evolution from the initial studies in molecular magnetism addressed mostly to simple dinuclear complexes, for which a detailed analysis of the correlation between the structure and the magnetic properties was usually scrutinized, and the present studies devoted to single-molecule magnets.[6,8] However, due to the structural complexity of the single molecule magnets and to the presence of many different exchange interactions within one such molecule, a detailed study of the exchange interactions in those systems is usually not undertaken. It must be recalled that for polynuclear complexes it is not possible in many cases to extract a set of exchange coupling constants (J) from the magnetic susceptibility data due to two fundamental problems: (i) the size of the system makes it impossible to perform a fitting with the current computational resources and (ii) the existence of many solutions that fit perfectly the experimental data makes uncertain which is the physically meaningful set of coupling constants.

The use of methods based on density functional theory using hybrid functionals provide J values in excellent agreement with the experimental data for transition metal complexes.[7,9] This approach allows us to obtain directly all the exchange coupling constants for such systems and, in some cases, the theoretical values can be employed to rule out unphysical sets of fitted J values. Despite the important role that the theoretical methods can play in this field, up to now this kind of studies have been basically employed to determine the J values or to just help to select a right set of fitted values, but not to obtain magneto-structural correlations, probably due to the complexity of the systems.[9] The analysis of magnetostructural correlations has also been limited by the lack of theoretical models for polynuclear complexes, in comparison with those employed for the dinuclear complexes, for which the Hay−Thibeault−Hoffmann (HTH)[10] and Kahn−Briat (KB)[11,12] models allow us to correlate the J values with the orbital energies and the overlap between “magnetic orbitals”, respectively. The butterfly complexes are based on the $[Fe_4O_2]^{8+}$ framework with two types of Fe^{III} cations (**1**), two placed at the body of the “butterfly” (Fe_b) and another two on the wingtips (Fe_w).

The present work has two goals. The first one is to study the magnetic properties of the Fe_4 butterfly complexes by analyzing in depth the structural dependence of the exchange coupling constants. The second goal is to develop a simple model that

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(1) Gatteschi, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 246.
(2) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873.
(3) Delfs, C.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Wieghardt, K.; Hanke, D. *Inorg. Chem.* **1993**, *32*, 3099.
(4) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.
(5) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 7124.
(6) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.
(7) Ruiz, E.; Alvarez, S.; Rodríguez-Fortea, A.; Alemany, P.; Pouillon, Y.; Massobrio, C. In *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2, p 227.
(8) Miller, J. S., Drillon, M., Eds. *Magnetism: Molecules to Materials*; Wiley-VCH: Weinheim, 2001−2005.; Vol. 1−5.
(9) Ruiz, E. *Struct. Bonding* **2004**, *113*, 71.
(10) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
(11) Kahn, O.; Briat, B. *J. Chem. Soc. Trans.* **1976**, *72*, 268.
(12) Kahn, O.; Briat, B. *J. Chem. Soc. Trans.* **1976**, *72*, 1441.

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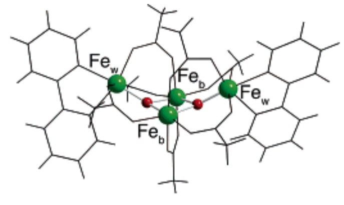

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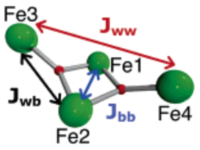
could help us understand the magnetostructural correlations in terms of electronic structure concepts, as done by the HTH and KB models for dinuclear complexes.[13−16] We have selected the Fe_4 butterfly complexes because such a tetranuclear unit appears also repeatedly in many iron complexes with larger nuclearity, such as Fe_6,[17] Fe_8,[3,18,19] Fe_{10},[20,21] and Fe_{19}[22−24] complexes.

Results and Discussion

Analysis of the Exchange Interaction in Fe_4 Butterfly Complexes. The spin Hamiltonian for a Fe_4 complex considering only the exchange coupling terms can be expressed as:

$$\hat{H} = -J_{wb}[\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4] - J_{bb}\hat{S}_1\hat{S}_2 - J_{ww}\hat{S}_3\hat{S}_4 \quad (1)$$

where $\hat{S}_i$ are the spin operators of each paramagnetic Fe^{III} center. There are four J_{wb} exchange interactions between one body iron atom (Fe_b) and one external atom (Fe_w) placed at the wingtip of the butterfly framework, connected trough a single μ_3-oxo bridging ligand, one J_{bb} interaction between the two body iron atoms coordinated by a double μ_3-oxo bridging ligand and, finally, the J_{ww} interaction between the two wingtip iron atoms trough the central Fe_2O_2 framework (**2**).



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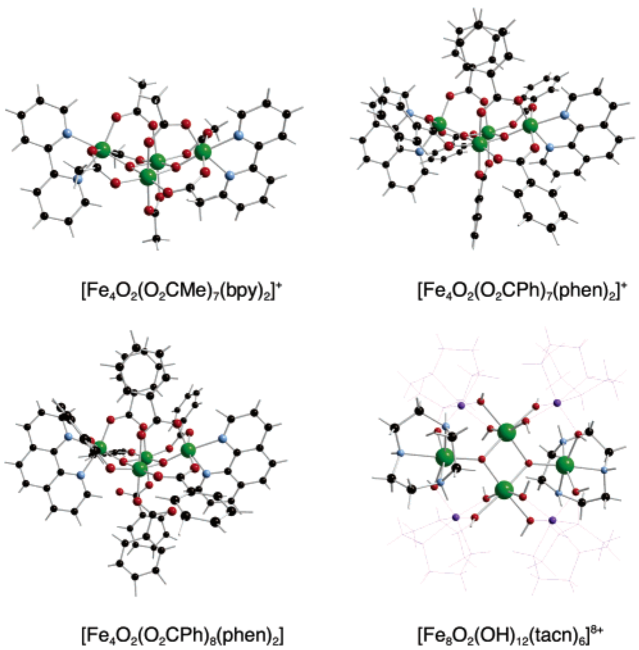
$[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$
$[Fe_4O_2(O_2CPh)_7(phen)_2]^+$
$[Fe_4O_2(O_2CPh)_8(phen)_2]$
$[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$

Figure 1. Representation of the molecular structures of the four studied Fe_4 complexes (see Table 1). In the case of a tacn−Fe_8 complex, the Fe_4 core studied is highlighted with ball and sticks. The nitrogen, oxygen, iron, and carbon atoms are represented by color spheres, blue, red, green, and black, respectively.

Table 1. Calculated *J* Values (cm^{-1}) Using B3LYP Functional for Different Fe_4 Complexes[a]

	Calculated			Experimental		
	J_{wb}	J_{bb}	J_{ww}	J_{wb}	J_{bb}	ref
$[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$	−80.0	8.3	−5.8	−91.0	−18.8	25
$[Fe_4O_2(O_2CPh)_7(phen)_2]^+$	−84.2	−0.9	−7.2	−77.6	−2.4	26
$[Fe_4O_2(O_2CPh)_8(phen)_2]$	−82.8	−15.2	−6.3	−65.7	−15.6	26
$[Fe_4O_2(OH)_{12}(tacn)_2]^{8+}$	−82.8	−7.6	−5.6	−	−	
$[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$	−66.5	5.1	−	−120	−25	18, 19

[a] See Computational Details for details. The results previously calculated with the same approach for the Fe_8 complex $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8{\cdot}9H_2O$ (tacn = 1,4,7-triazacyclononane) are also given.[18,19] The available results obtained from a fitting of the experimental magnetic susceptibility curve are also indicated. For the Fe_8 complex, the experimental values are just a guess because the fitting cannot be done due to the large size of the system (see ref 19 for a detailed discussion).

The calculated *J* values for three Fe_4 complexes and one Fe_4 model cut out from an Fe_8 structure (Figure 1) are presented in Table 1. From the experimental point of view, usually only two *J* values (J_{wb} and J_{bb}) have been employed in the literature, due to the difficulties to perform a fitting with many *J* values. In contrast, with DFT calculations we can indeed obtain directly the three *J* values. Moreover, due to the presence of four J_{wb} interactions and only one each of J_{ww} and J_{bb} interactions, it is practically impossible to obtain accurate values for these two because the magnetic susceptibility is insensitive to large variations of J_{bb} (see Supporting Information).[25]

From the analysis of our results, the following conclusions can be drawn: (i) The J_{wb} coupling constant is moderately antiferromagnetic and corresponds to the strongest interaction,

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(13) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.
(14) Desplanches, C.; Ruiz, E.; Rodríguez-Fortea, A.; Alvarez, S. *J. Am. Chem. Soc.* **2002**, *124*, 5197.
(15) Blanchet-Boiteux, C.; Mouesca, J. M. *Theor. Chem. Acc.* **2000**, *104*, 257.
(16) Blanchet-Boiteux, C.; Mouesca, J. M. *J. Phys. Chem. A* **2000**, *104*, 2091.
(17) Harding, C. J.; Henderson, R. K.; Powell, A. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 570.
(18) Barra, A. L.; Gatteschi, D.; Sessoli, R. *Chem.−Eur. J.* **2000**, *6*, 1608.
(19) Ruiz, E.; Cano, J.; Alvarez, S. *Chem.−Eur. J.* **2005**, *11*, 4767.
(20) Parsons, S.; Solan, G. A.; Winpenny, R. E. P.; Benelli, C. *Angew. Chem., Int. Ed.* **1996**, 1825.
(21) Rajaraman, G.; Ruiz, E.; Cano, J.; Alvarez, S. *Chem. Phys. Lett.* **2005**, *415*, 6.
(22) Goodwin, J.; Sessoli, R.; Gatteschi, D.; Wernsdorfer, W.; Powell, A. K.; Heath, S. L. *J. Chem. Soc. Dalton Trans.* **2000**, 1835.
(23) Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491.
(24) Ruiz, E.; Rodríguez-Fortea, A.; Cano, J.; Alvarez, S. *J. Phys. Chem. Solids* **2003**, *65*, 799.
(25) 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.
(26) Boudalis, A. K.; Lalioti, N.; Spyroulias, G. A.; Raptopoulou, C. P.; Terzis, A.; Bousseksou, A.; Tangoulis, V.; Tuchagues, J. P.; Perlepes, S. P. *Inorg. Chem.* **2002**, *41*, 6474.
(27) Wemple, M. W.; Coggin, D. K.; Vincent, J. B.; McCusker, J. K.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc. Dalton Trans.* **1998**, 719.
(28) Yan, B.; Chen, Z. D. *Inorg. Chem. Commun.* **2001**, *4*, 138.
(29) Overgaard, J.; Hibbs, D. E.; Rentschler, E.; Timco, G. A.; Larsen, F. K. *Inorg. Chem.* **2003**, *42*, 7593.
(30) Boudalis, A. K.; Tangoulis, V.; Raptopoulou, C. P.; Terzis, A.; Tuchagues, J. P.; Perlepes, S. P. *Inorg. Chim. Acta* **2004**, *357*, 1345.
(31) Glaser, T.; Lugger, T. *Inorg. Chim. Acta* **2002**, *337*, 103−112.
(32) Chaudhuri, P.; Rentschler, E.; Birkelbach, F.; Krebs, C.; Bill, E.; Weyhermuller, T.; Florke, U. *Eur. J. Inorg. Chem.* **2003**, 541.
(33) Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77.

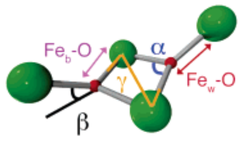
Table 2. Average Bond Distances (Å) and Bond Angles (deg) Employed in the Magnetostructural Correlations of the Fe_4 Complexes[a,b]

	Fe_b–O	Fe_w–O	α	β	γ	J_{wb}	J_{bb}	ref
$[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$	1.94	1.82	95	31	12	−91.0	−18.8	25
$[Fe_4O_2(O_2CMe)_6(bpy)_2]^{2+}$	1.96	1.82	95	48−17	25	−82.0	−21.8	27
$[Fe_4O_2(O_2CEt)_7(bpy)_2]^+$	1.94	1.82	96	31	0	−83.2	−14.6	28
$[Fe_4O_2(O_2CPh)_7(phen)_2]^+$	1.93	1.81	96	25	10	−77.6	−2.4	26
$[Fe_4O_2(O_2CPh)_8(phen)_2]$	1.95	1.82	97	29	7	−65.7	−15.6	26
$[Fe_4O_2(O_2CCMe_3)_8(NC_5H_4Me)_2]$	1.94	1.85	99	32	0	−74.4	–	29
$[Fe_4O_2(O_2CMe)_6(N_3)_2(phen)_2]$	1.95	1.83	95	39−12	19	−70.0	−11.0	30
$[Fe_4(HL)_6(acac)_2](NEt_4)_3Cl$	1.97	1.86	92	30	20	−92.0	–	31
$[Fe_4O_2(salox)_2(dpg)_3L'_2]ClO_4$	1.97	1.87	92	28	33	−82.8	–	32
$[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$	1.96	1.86	97	17	3	–	–	33

[a] α, β, and γ correspond to the Fe_b−O−Fe_b bond angle, the out-of-plane shift of the Fe_w atoms, and the dihedral Fe_b−O−Fe_b−O angle, respectively. For significantly asymmetric complexes, the two different β values are given. The available experimental J values are also shown (in cm^{-1}). [b] L = 2,6-bis(oxymethyl)-4-tert-butylphenol; L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane; salox = salicylaldoximato dianion; dpg = diphenylglycolate

showing in all cases very good agreement between experimental and theoretical values. Moreover, the calculated J_{wb} values are very similar for all the studied tetranuclear complexes. (ii) The body−body interactions can be weakly ferromagnetic or antiferromagnetic, showing important differences among the studied complexes. (iii) The wing−wing coupling constants show very similar weak antiferromagnetic values for all the complexes, similar in strength to those corresponding to the body−body interaction. (iv) The wing−wing interaction are non-negligible, contrary to what is usually assumed for fitting the experimental data. (v) The results for the Fe_4 model of an Fe_8 complex and those for the whole structure (see Table 1) show non-negligible differences, a weaker wing−body interaction, and a change in the nature of the body−body interaction, being ferromagnetic for the Fe_8 complex such as in one of the calculated Fe_4 complexes. These results indicate the high sensitivity of the J values to modifications in the structure, i.e., the elimination of the four external iron atoms in the Fe_8 complex importantly affects the central body−body interaction. (vi) The relative strengths of the different types of interaction are in agreement with similar results obtained by us for other polynuclear iron compounds such as Fe_8, Fe_{19}, Fe_{10}, and Fe_{11} complexes, the interactions through single μ_3-oxo bridges being stronger than those corresponding to the double bridges.[9,21,24]

Magnetostructural Correlations in Fe_4 Butterfly Complexes. We have analyzed the variations of the structural parameters in the Fe_4 butterfly complexes reported in the literature, as well as the dependence of the exchange coupling constants on five structural parameters (see **3** and Table 2). To understand such a structural dependence of the J values, we have carried out calculations for a model structure (Fe_b−O = 1.94 Å, α = 96°; Fe_w−O = 1.84 Å, β = 20° and γ = 0°) in which these parameters were varied to cover the experimental range of values.



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The analysis of the theoretical results for the magnetostructural correlations (Figures 2 and 3) indicates a stronger dependence of the J values with two structural parameters, the Fe_b−O bond distance and the α Fe_b−O−Fe_b angle (Figure 2). From these results, we can extract some trends: (i) There is a strong dependence of the wing−body interaction on the Fe_b−O bond distance: shorter Fe_b−O bond distances and larger α angles give rise to stronger wing−body interactions. All the experimental Fe_b−O bond distances and Fe_b−O−Fe_b bond angles appear in a narrow range of values, explaining the small variation of experimental and theoretical J_{wb} values. (ii) The body−body interaction also presents relatively important changes with these two structural parameters, showing that a ferromagnetic behavior could appear for long Fe_b−O bond distances. The strong wing−body interaction forces the two central Fe_b atoms to have the same spin sign, producing spin frustration when the J_{bb} interaction is antiferromagnetic. The parabolic dependence of the J_{bb} exchange constant on the Fe_b−O−Fe_b bond angle is similar to that found in dinuclear copper complexes on the Cu−O−Cu bond angle.[13] (iii) The wing−wing interaction is less affected by geometrical changes and

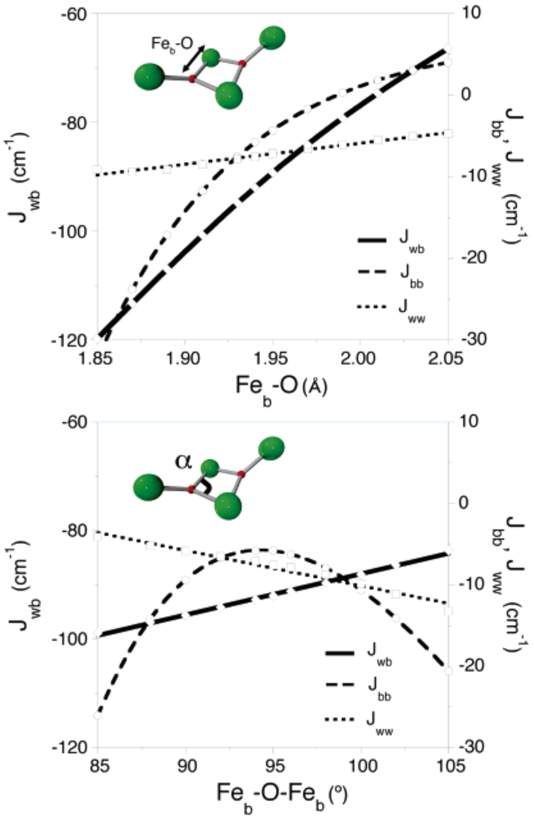

Figure 2. Dependence of the exchange coupling constants on the Fe_b−O bond distance and the Fe_b−O−Fe_b angle.

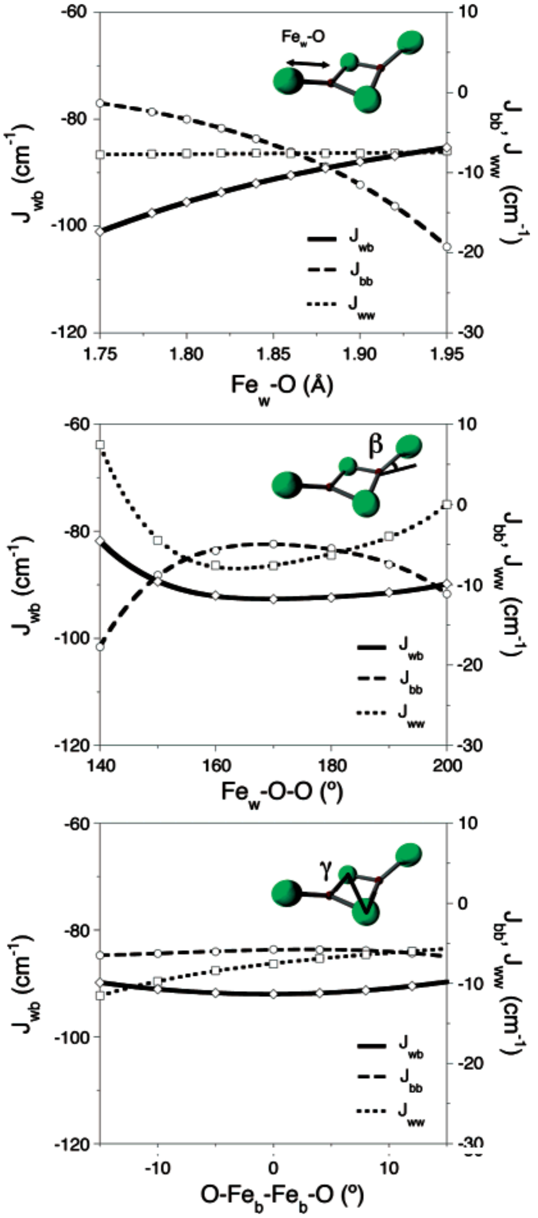

Figure 3. Dependence of the exchange coupling constants with the Fe_w-O bond distance, the out-of-plane shift of the Fe_w atoms, and the dihedral Fe_b-O-Fe_b-O angles.

the J_{ww} values remain in the region of weak antiferromagnetic coupling for the whole range of explored geometrical parameters.

The dependence of the exchange coupling constants on the Fe_w-O bond distance, the out-of-plane shift of the Fe_w atoms (β), and the dihedral Fe_b-O-Fe_b-O angle (γ) is considerably smaller than those on the Fe_b-O bond distance and Fe_b-O-Fe_b bond angle (Figure 3). It is worth noting some surprising results that prove the subtle interplay of factors that control the exchange interactions, i.e., changes in the Fe_w-O bond distance have a larger influence on the J_{wb} and J_{bb} values than on the wing−wing interaction.

Theoretical Models for Magnetostructural Correlations. To analyze the magnetostructural correlations, we have employed the same models that have been extensively applied to dinuclear complexes. Thus, the Hay−Thibeault−Hoffman model correlates the exchange coupling constants with the energy gap of the molecular orbitals bearing the unpaired electrons,[10] whereas the Kahn−Briat model[6,11,12] correlates the J's with the overlap between the localized "magnetic orbitals" of the paramagnetic centers.

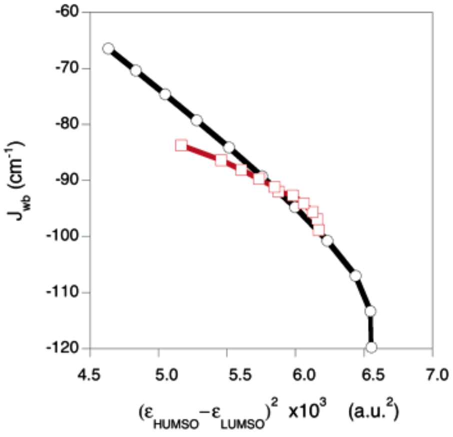

Figure 4. Dependence of the exchange coupling constants J_{wb} on the Fe_b-O bond distance (○) and of the Fe_b-O-Fe_b angle (□) on the square of the energy difference between the highest and lowest UMSOs (unoccupied magnetic spin orbitals) with significant contribution at all four Fe^{III} cations.

The set of the occupied α orbitals shows a complicated picture because of extensive mixing that prevents the identification of the twenty molecular orbitals bearing the unpaired electrons in a Fe_4 butterfly complex. However, in the case of the empty β molecular orbitals corresponding to the high spin solution (called UMSO,[14] unoccupied magnetic spin orbitals), such orbitals can be properly assigned. Previously, we and other authors have found for other systems that the empty β spin orbitals provide a better qualitative description than the equivalent α orbitals.[14,15] In the present case, we find a correlation between the values of the strongest coupling constants (J_{wb}) and the energy of such orbitals (Figure 4). To simplify the orbital analysis of the large number of orbitals involved, we have selected the highest and lowest orbitals with contributions at both body and wing Fe^{III} cations (Figure 5). Such an approach is similar to that applied for solid-state compounds, for which the bandwidth is employed for the correlations.[34,35] We obtained a reasonable correlation between the J_{wb} value and the square of the orbital energy difference (Figure 4). The variations of the two geometrical parameters, the Fe_b-O bond distance and the Fe_b-O-Fe_b angle, give similar orbital energy differences. As expected, an increase of the energy difference results in a stronger antiferromagnetic contribution.

The two orbitals involved in the correlation are represented in Figure 5. The highest energy orbital (Figure 5, above) has a nonbonding Fe_b-O character, hence, its energy remains almost unchanged when the Fe_b-O bond distance and the Fe_b-O-Fe_b angle are varied. In contrast, the lowest energy orbital (Figure 5 below) has a bonding Fe_b-O character and, consequently, its energy increases for longer Fe_b-O bond distances, resulting in a smaller orbital energy difference and a decreased J_{wb} value (Figure 2). The increase of the Fe_b-O-Fe_b angle apparently would cause a stabilization of this orbital due to a better overlap between the Fe_b and O orbitals; however, there is an important increase in the contribution of the oxygen p

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(34) Girerd, J. J.; Charlot, M.-F.; Kahn, O. *Mol. Phys.* **1977**, *34*, 1063.
(35) Charlot, M.-F.; Girerd, J. J.; Kahn, O. *Phys. Status Solidi B* **1978**, *86*, 497.

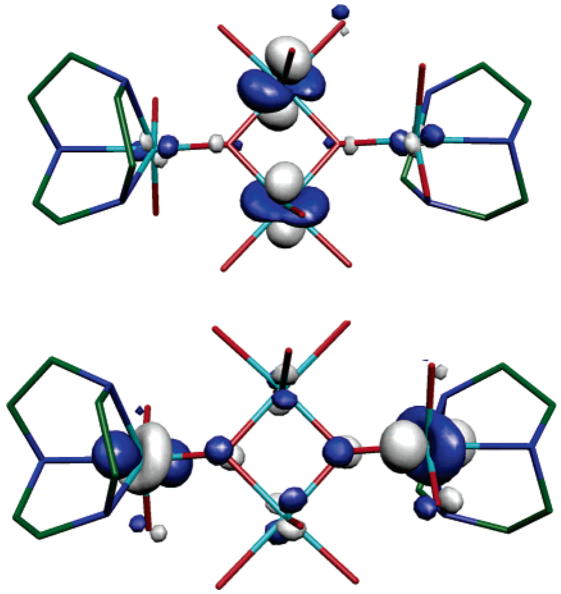

Figure 5. Representation of the two empty β orbitals (UMSOs) with highest and lowest energies that have significant contribution at the four Fe^{III} cations.

orbitals that increases the energy due to the antibonding Fe$_w$−O interaction. Hence, the increase of the Fe$_b$−O−Fe$_b$ angle also reduces the orbital energy difference giving a smaller antiferromagnetic J_{wb} constant (Figure 2).

The Kahn−Briat model relates the antiferromagnetic contribution of the exchange coupling constant between two paramagnetic centers with the overlap between the orbitals bearing the unpaired electrons. Such "magnetic orbitals" are those corresponding to the fragment of each paramagnetic metal cation and their ligands. Thus, using this model we can predict for instance in the case of a dinuclear Cr^{III}Ni^{II} complex that the coupling will be ferromagnetic because the overlap between magnetic orbitals of the Cr^{III} cation with t_{2g} symmetry, assuming an octahedral coordination of the metals, and those with e_g symmetry of the Ni^{II} cation should be practically zero, resulting in a very small antiferromagnetic contribution. A representation of such localized magnetic orbitals can be obtained from the calculations using the orbitals obtained from the broken-symmetry solution for a dinuclear complex taking the alpha orbitals bearing the unpaired electrons localized on one paramagnetic atom and the beta ones for the other metal.[14] Due to the nature of the broken-symmetry wavefunctions, such orbitals are non-orthogonal, giving a procedure to obtain a correlation using the Kahn−Briat model and the orbitals obtained from a DFT calculation. On the other hand, the direct application of the Kahn−Briat model becomes unpractical for polynuclear complexes because it is not possible to obtain localized non-orthogonal "magnetic orbitals" on each paramagnetic center directly from the DFT calculations as done previously for dinuclear complexes. As an alternative, we have previously obtained an approximate mathematical expression that relates the overlap between "magnetic orbitals" and the spin populations at the paramagnetic centers.[36,37] In the Supporting Information, we have extended such a mathematical relationship for any number of unpaired electrons at the paramagnetic centers, obtaining the following expression:

$$\Delta_{AB} = \left(\sqrt{(\rho^{A}_{HS})^2 - (\rho^{A}_{LS})^2} + \sqrt{(\rho^{B}_{HS})^2 - (\rho^{B}_{LS})^2}\right)^2 = 4n \sum_{i=1}^{n} \langle a_i | b_i \rangle^2 \qquad (2)$$

where $\rho^{A,B}_{HS,LS}$ are the different spin populations of the paramagnetic centers A or B involved in the exchange interaction in the highest (HS) or lowest spin (LS) configurations, n is the number of unpaired electrons at paramagnetic centers A and B, and a_i and b_i are the magnetic orbitals analogous to those proposed in the Kahn−Briat model.[6,11,12] Thus, according to eq 2, the strength of the exchange coupling should be linearly dependent on Δ_{AB}, as nicely found for the wing−body interaction (Figure 6). A similar linear correlation is obtained between the two magnitudes independently of the approach employed for the calculation of spin populations, Mulliken, or natural bond orbitals (NBO).[38] These results show that an increase of the difference of the spin population between the high and low spin wavefunction at one paramagnetic center is associated with a stronger antiferromagnetic coupling.

Spin Density Distribution in Fe$_4$ Butterfly Complexes. The spin density distributions corresponding to the $S = 0$ ground state are very similar in all the studied cases. One of them is shown in Figure 7. Due to the d^5 electronic configuration of the Fe^{III} cations, the spin distribution is almost spherical at the paramagnetic centers[39] and the delocalization mechanism is predominant at the ligand atoms coordinated to the metals.[40,41] The spin population on the iron atoms is around 4.2 e$^-$, and the missing spin density, relative to five unpaired electrons, appears delocalized over the ligands. In the central oxygen atoms, there are two lobes with spin densities of different sign that appear due to the presence of two neighboring Fe^{III} cations with opposite spin density, and probably this spin density is an artifact due to the single-determinant wavefunction considered in this case.

Concluding Remarks

The exchange coupling constants and magnetostructural correlations in Fe$_4$ butterfly complexes have been studied using theoretical methods based on density functional theory. The results show the presence of three different coupling constants, and the strongest interaction is an antiferromagnetic coupling between body (Fe$_b$) and wing iron (Fe$_w$) atoms through a μ_3-oxo bridging ligand as found experimentally. The wing−wing interactions, usually neglected in the fitting of the experimental susceptibility data, show a weak antiferromagnetic coupling of similar magnitude in all the complexes. Finally, the body−body interaction can be ferromagnetic or antiferromagnetic depending on the structural parameters. The analysis of the dependence of the exchange coupling constants on the structural parameters indicates a relatively strong dependence of the wing−body and body−body interactions with the Fe$_b$−O bond distance and the Fe$_b$−O−Fe$_b$ angle.

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(36) Ruiz, E.; Rodríguez-Fortea, A.; Alvarez, S.; Verdaguer, M. *Chem.*−*Eur. J.* **2005**, *11*, 2135.
(37) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comp. Chem.* **1999**, *20*, 1391.
(38) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(39) Ruiz, E.; Cirera, J.; Alvarez, S. *Coord. Chem. Rev.* **2005**, *249*, 2649.
(40) Cano, J.; Ruiz, E.; Alvarez, S.; Verdaguer, M. *Comments Inorg. Chem.* **1998**, *20*, 27.
(41) Ruiz, E.; Alvarez, S. *ChemPhysChem* **2005**, *6*, 1094.

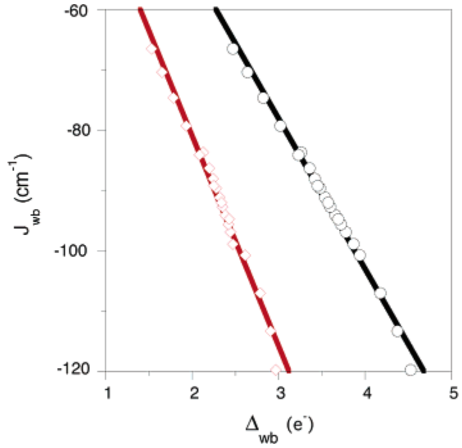


Figure 6. Dependence of the J_{wb} coupling constants calculated with different Fe$_b$−O bond distances and Fe$_b$−O−Fe$_b$ angles, on Δ_{AB} (eq 2). Mulliken (◊) and natural bond orbital (NBO, ○) results are shown.

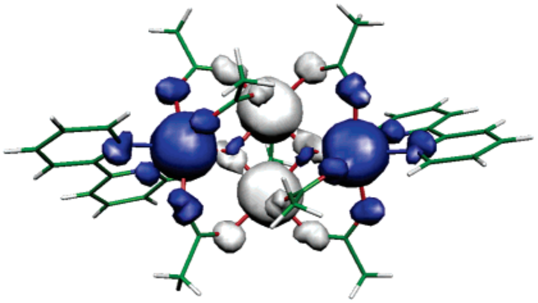


Figure 7. Spin density distribution for $[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$ corresponding to the $S = 0$ single-determinant solution of the ground state. The isodensity surface represented corresponds to a value of 0.005 e$^-$/bohr^3 (positive and negative values are represented as white and blue surfaces, respectively).

The applicability of the Hay−Thibeault−Hoffmann and Kahn−Briat models for these polynuclear complexes has been studied. The large mixing of the occupied orbitals prevents a clear-cut identification of the singly occupied orbitals. Hence, we employed the β unoccupied magnetic orbital corresponding to the high spin wavefunction and found that the strongest J_{wb} has an approximately linear correlation with the square of the energy difference between the lowest and highest unoccupied magnetic orbitals. In the case of the Kahn−Briat model, it is not possible to obtain perfectly localized non-orthogonal magnetic orbitals from the calculations. Thus, we have obtained a mathematical expression that allows us to estimate the overlap between such orbitals from the calculated spin populations of the paramagnetic centers. Using such an expression, we found a nice linear correlation between J_{wb} and the square of the overlap of the magnetic orbitals, as predicted by the Kahn−Briat model.

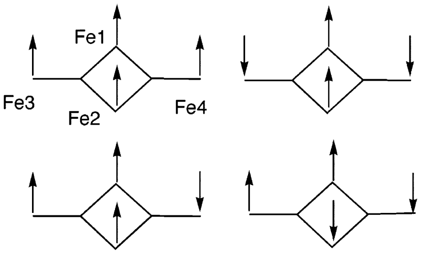
Computational Details

Gaussian03 calculations[42] were performed using the quadratic convergence approach with the hybrid B3LYP functional[43] and a guess function generated with the Jaguar 6.0 code.[44] A triple-ζ all-electron Gaussian basis set has been used for the iron atoms,[45] and a double-ζ basis set has been used for the other elements.[46]

Because a detailed description of the computational strategy adopted in this work can be found elsewhere,[37,47,48] we will only sketch briefly its most relevant aspects here. A phenomenological Heisenberg Hamiltonian is used, excluding the terms related with the magnetic anisotropy, to describe the exchange coupling in the polynuclear complex:

$$\hat{H} = -\sum_{a<b} J_{ab}\hat{S}_a\hat{S}_b \tag{3}$$

where $\hat{S}_a$ and $\hat{S}_b$ are the spin operators of the different paramagnetic centers. The J_{ab} parameters are the pairwise coupling constants between the paramagnetic centers of the molecule. Basically, we need to calculate the energy of $n + 1$ spin distributions for a system with n different exchange coupling constants. These energy values allow us to build up a system of n equations in which the J values are the unknowns. In the present study, the four calculations performed to obtain the three exchange coupling constants J_{wb}, J_{bb}, and J_{ww} correspond to the high spin $S = 10$ solution, an $S = 0$ solution with Fe3 and Fe4 having down spin, an $S = 0$ solution with Fe2 and Fe4 having down spin, and an $S = 5$ configuration in which only the Fe4 has down spin (**4**). We have included a fifth spin distribution ($S = 5$, Fe2 spin down) to analyze possible changes in the calculated J values, however, the obtained results are almost identical. One of the Fe$_4$ complexes[25] was previously used to verify some of the procedures employed in the calculations, such as functionals, basis sets, and computational parameters in numerical DFT calculations.[49]



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Supporting Information Available: Representation of the χT values for three different sets of J values for an Fe$_4$ butterfly complex. Detailed mathematical description of eq 2 that relates the overlap between magnetic orbitals and the spin populations, and ref 42 in full. Cartesian coordinates and calculated energies of the employed models. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Frisch, M. J.; et al. *Gaussian 03*, revision C.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(43) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648

(44) *Jaguar 6.0*; Schrödinger, LLC: New York, 2005

(45) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829

(46) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571

(47) Ruiz, E.; Alvarez, S.; Cano, J.; Polo, V. *J. Chem. Phys.* **2005**, *123*, 164110.

(48) Ruiz, E.; Rodríguez-Fortea, A.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comp. Chem.* **2003**, *24*, 982.

(49) Ruiz, E.; Cauchy, T.; Tercero, J.; Rodríguez-Fortea, A.; Massobrio, C. *J. Chem. Phys.* **2005**, *123*, 074102.