

Theoretical Study of the Magnetic Behavior of [Fe₈] and [Fe₁₆] WheelsRosa Carrasco,[†] Joan Cano,^{*‡} Talal Mallah,[‡] Leigh F. Jones,[§] David Collison,[§] and Euan K. Brechin^{*§}

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The reaction of the trimetallic species [Fe₃O(PhCOO)₆(H₂O)₃]NO₃ with 1,1,1-tris(hydroxymethyl)ethane (H₃thme) affords either the octametallallic species [Fe₈(PhCOO)₁₂(thme)₄] **1** or the hexadecametallic species [Fe₁₆(EtO)₄(PhCOO)₁₆(Hthme)₁₂](NO₃)₄ **2**, depending on the nature of the solvent used for crystallization. The structure of **1** can be described as a nonplanar wheel of eight Fe^{III} ions bridged by a combination of PhCOO⁻ and thme³⁻ ligands, and **2** as a nonplanar wheel of sixteen Fe^{III} ions bridged by PhCOO⁻, Hthme²⁻, and EtO⁻ ligands. Both compounds can be broken down into simple units of two metal ions and the bridging ligands that connect them. The best fits of the χ vs T curves in the 300–10 K temperature range were obtained with the parameters $g = 2.0$, $J_1 = -24.0$ cm⁻¹, and $J_2 = -8.59$ cm⁻¹ for [Fe₈] and $g = 2.0$, $J_1 = -25.0$ cm⁻¹, $J_2 = -11.73$ cm⁻¹, and $J_3 = -69.3$ cm⁻¹ for [Fe₁₆]. Density functional theory (DFT) calculations show that the antiferromagnetic interactions between the metals in the dinuclear units decrease when two types of bridging ligands are present, as expected for an orbital counter-complementarity effect.

Introduction

The study of the magnetic behavior of large metal clusters is a topic of great current interest.¹ Much of this has resulted from the discovery that some metal clusters that have a large spin ground state and a significant negative zero-field splitting of that ground state possess a molecular magnetic memory effect.² An intriguing class of cluster in this respect is the “molecular wheel”. Most even-membered wheels are antiferromagnetic and characterized by $S = 0$ ground states,³ and although they cannot function as single-molecule magnets (SMMs), they represent ideal model systems for the study of one-dimensional (1-D) magnetic materials, quantum effects, and magnetic anisotropy.⁴

We have been investigating the chemistry of the pro-ligand 1,1,1-tris(hydroxymethyl)ethane (H₃thme) and its analogues

in the synthesis of novel transition metal clusters with Mn,⁵ Ni,⁶ Co,⁷ and Fe.⁸ We previously communicated the synthesis of the two Fe^{III} wheels [Fe₈] **1** and [Fe₁₆] **2**,⁹ and now we report a detailed study of their magnetic properties.

Experimental Section

Computational Details. A detailed description of the computational strategy adopted in this work has been described elsewhere¹⁰ and is only briefly reviewed here. For the evaluation of the coupling constant of dinuclear models, two separate calculations are carried out by means of density functional theory,¹¹ one for the triplet and another for the singlet state. The hybrid B3LYP method,¹² as implemented in Gaussian98,¹³ has been used in all calculations,

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- (1) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.
- (2) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Følting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816.
- (3) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823.
- (4) Meier, F.; Loss, D. *Phys. Rev. B* **2001**, *64*, 224411/1.

- (5) Brechin, E. K.; Soler, M.; Davidson, J.; Hendrickson, D. N.; Parsons, S.; Christou, G. *Chem. Commun.* **2002**, 2252.
- (6) Moragues Canovas, M.; Helliwell, M.; Ricard, L.; Rivière, É.; Wernsdorfer, W.; Brechin, E. K.; Mallah, T. *Eur. J. Inorg. Chem.* **2004**, 2219.
- (7) Moragues Canovas, M.; Brechin, E. K.; Mallah, T. Unpublished results.
- (8) Jones, L. F.; Brechin, E. K.; Collison, D.; Helliwell, M.; Mallah, T. *Inorg. Chem.* **2003**, *42*, 6601.
- (9) Jones, L. F.; Batsanov, A.; Brechin, E. K.; Collison, D.; Helliwell, M.; Mallah, T.; McInnes, E. J. L.; Piligkos, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4318.
- (10) Ruiz, E.; Rodríguez-Fortea, A.; Cano, J.; Alvarez, S. *J. Comput. Chem.* **2003**, *24*, 982.
- (11) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

mixing the exact Hartree–Fock exchange¹⁴ with Becke's expression for the exchange and with the Lee–Yang–Parr correlation functional.¹⁵ Double- ζ quality and triple- ζ quality basis sets proposed by Ahlrichs and co-workers¹⁶ have been employed for non-metal and metal atoms, respectively. For the metal atoms, we have also added two extra polarization p functions. The presence of a low-energy excited singlet makes it difficult to accurately evaluate the energy of the lowest singlet by a single-determinant method. To solve this problem, broken-symmetry wave functions, as proposed by Noodleman et al., have been used.^{17–20} Previously, it has been found that, among the most common functionals, the B3LYP method combined with the broken-symmetry treatment is the strategy that provides the best results for calculating coupling constants.^{10,21–23} It is clear that for broken-symmetry Hartree–Fock calculations it is necessary to make a correction due to the multideterminant character of the wave function of the low-multiplicity state.²³ On the other hand, for DFT calculations we adopt single-determinant wave functions for which DFT is well-defined.^{24–26} Then, we use the broken-symmetry energy calculated by DFT methods as the real energy of the state.

Structural Descriptions. The structure of $[Fe_8(PhCOO)_{12}(thme)_4]$ **1** (Figure 1) can be described as a wheel of eight Fe^{III} ions bridged by a combination of $PhCOO^-$ and $thme^{3-}$ ligands. The $PhCOO^-$ ligands bridge neighboring Fe^{III} ions in their usual μ -manner, while the triply deprotonated $thme^{3-}$ ligands show much greater flexibility in each bridging four iron centers, with each arm providing a μ_2 -oxygen for adjacent iron centers. Thus each Fe center in **1** is bridged to its neighbor either by two alkoxides and one carboxylate or by one alkoxide and two carboxylates. The structure of $[Fe_{16}(EtO)_4(PhCOO)_{16}(Hthme)_{12}(NO_3)_4]$ **2** (Figure 2) is best described as a wheel of sixteen Fe^{III} ions bridged by $PhCOO^-$, $Hthme^{2-}$, and EtO^- ligands. The $PhCOO^-$ again bridge in their familiar μ_2 mode, but in this structure the tripodal ligands are only doubly deprotonated ($Hthme^{2-}$). Eight of these ligands use their two deprotonated arms as μ_2 bridges, forming a nearly linear chain of three metals, with the third protonated arm bonded only to the central iron center. Four $Hthme^{2-}$ ligands occupy the central cavity of the wheel: the deprotonated arms again acting as μ_2 bridges,

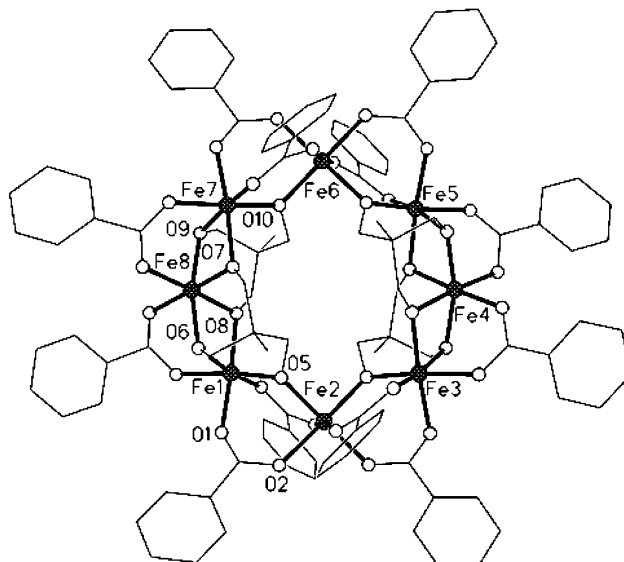


Figure 1. Structure of **1**.

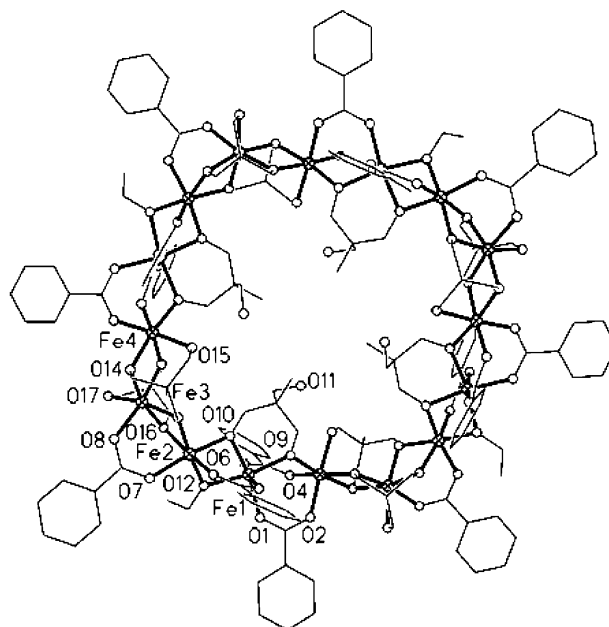


Figure 2. Structure of **2**.

with the protonated arm hydrogen bonding to the monodentate arm of an adjacent $Hthme^{2-}$ ligand and to a water molecule above the central cavity of the wheel. There are now also four EtO^- ligands present, each bridging two iron centers on the outside edge of the wheel. The result is that each Fe center in **2** is bridged either by two alkoxides and one carboxylate, by one alkoxide and two carboxylates, or solely by two alkoxides.

Results and Discussion

Initial studies of the magnetic behavior for both complexes showed the presence of dominant antiferromagnetic interactions, suggesting $S = 0$ ground states.⁹ Herein we analyze the data in more detail. Both **1** and **2** can be broken down into simple units of two metal ions and the bridging ligands that connect them. These simple units will be referred to as “basic interaction units” (BIU). Despite the small structural changes between similar BIU, **1** and **2** could be modeled

- (13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* (Revision A.7); Gaussian, Inc.: Pittsburgh, PA, 1998.
- (14) Becke, A. D. *J. Phys. Rev.* **1988**, *A38*, 3098.
- (15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
- (16) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
- (17) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mousesca, J. M. *Coord. Chem. Rev.* **1995**, *144*, 199.
- (18) Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423.
- (19) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 1.
- (20) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.
- (21) Cano, J.; Alemany, P.; Alvarez, S.; Verdaguer, M.; Ruiz, E. *Chem. Eur. J.* **1998**, *4*, 476.
- (22) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122.
- (23) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.
- (24) Perdew, J. P.; Savin, A.; Burke, K. *Phys. Rev. A* **1995**, *51*, 4531.
- (25) Miehlich, B.; Stoll, H.; Savin, A. *Mol. Phys.* **1997**, *91*, 527.
- (26) Goursot, A.; Malrieu, J. P.; Salahub, D. R. *Theor. Chim. Acta* **1995**, *91*, 225.

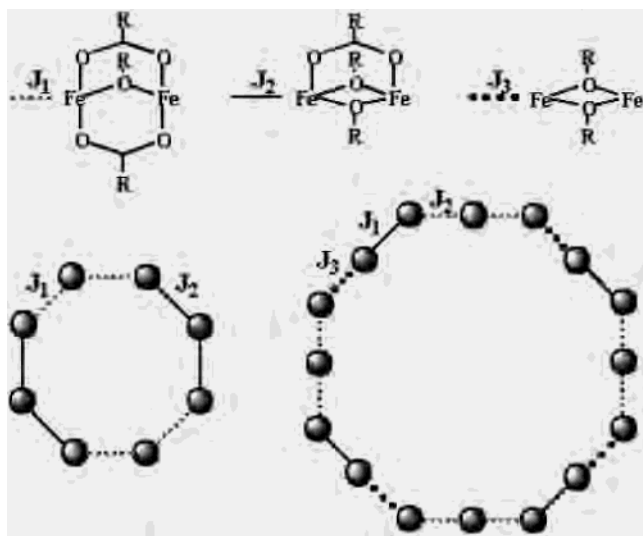


Figure 3. Scheme of the exchange interactions in Fe_8 (**1**) and Fe_{16} (**2**). The three different basic interaction units are shown.

following the interaction schemes shown in Figure 3. In these schemes, J_1 , J_2 , and J_3 are the magnetic coupling constants between two Fe^{III} ions, for each one of the three different BIU found in these systems. These three BIU have different kinds and numbers of bridging ligands. Thus, BIU1 represents one alkoxo and two carboxylate bridging ligands (J_1); BIU2 represents two alkoxo and one carboxylate bridging ligands (J_2); and BIU3 represents only two alkoxo bridging ligands (J_3).

To analyze the magnetic behavior of **1** and **2**, we have found exact analytical equations for the χT product as a function of the temperature, using the interaction topologies shown in Figure 3 and the phenomenological Heisenberg Hamiltonian $\hat{H} = -J\sum_{i,j} S_i S_j$. These equations have been developed following the classical spin approach and the methodology previously described by Fisher for one-dimensional systems.²⁷ This methodology can be applied since the spin correlation paths generated by the interaction schemes shown in Figure 3 are large enough to neglect spin autocorrelation contributions through an entire loop.²⁸ The obtained analytical laws are shown in the electronic Supporting Information.

Fits of the molar magnetic susceptibility curves, χ vs T , have been performed by use of the Mathematica package.²⁹ The fit obtained for **1** is unique, but in the case of compound **2** two sets of values have been obtained from the fit of the χ vs T curve, for different starting values of J_1 , J_2 , and J_3 . One of these two sets has been discarded, however, because the g -factor obtained for the Fe^{III} ions is too big (2.13). Moreover, the agreement factor of the fit, defined as $F = \{\sum[\chi_{\text{exptl}}(i) - \chi_{\text{calcd}}(i)]^2\} / \{\sum[\chi_{\text{calcd}}(i)]^2\}$, is rather worse than that obtained for the other set.

From an analysis of the molar magnetic susceptibility curve, χ vs T , the interaction topology of **1** does not allow

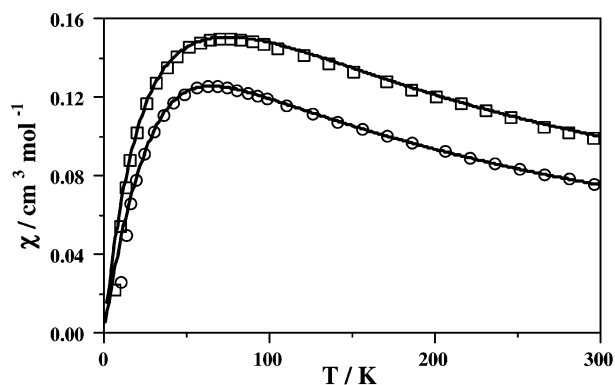


Figure 4. Experimental and theoretical (solid lines) χT vs T curves for Fe_{16} (\square) and Fe_8 (\circ).

us to assign the J_1 and J_2 values to the found constants. However, in the interaction topology associated with **2**, J_2 is more prevalent than J_1 and J_3 , so the analysis of the χ vs T curve of this compound allows us to assign a value for the J_2 coupling constant but not for J_1 and J_3 . The value of J_2 obtained for **2** helps us to assign a value for J_1 and J_2 in **1**. In the same way, the J_1 and J_2 values in **1** help us to find the values for J_1 and J_3 in **2**. Thus, the best fits of the χ vs T curves (Figure 4) in the 300–10 K temperature range are obtained with the following parameters: $g = 2.000 \pm 0.004$, $J_1 = -24.0 \pm 0.3 \text{ cm}^{-1}$, and $J_2 = -8.59 \pm 0.06 \text{ cm}^{-1}$ ($F = 1.4 \times 10^{-5}$ and $R^2 = 0.9995$) for **1** and $g = 2.000 \pm 0.003$, $J_1 = -25.0 \pm 0.8 \text{ cm}^{-1}$, $J_2 = -11.73 \pm 0.04 \text{ cm}^{-1}$, and $J_3 = -69.3 \pm 1.2 \text{ cm}^{-1}$ ($F = 8.9 \times 10^{-6}$ and $R^2 = 0.9998$) for **2**. This assignment is in agreement with the J values found for the previous $[\text{Fe}_{10}]$ ($J_2 = -9.8 \text{ cm}^{-1}$), $[\text{Fe}_{12}]$ ($J_2 = -10.1 \text{ cm}^{-1}$ and $J_2 = -15.8 \text{ cm}^{-1}$), and $[\text{Fe}_{18}]$ ($J_1 = -19.1 \text{ cm}^{-1}$ and $J_2 = -8.0 \text{ cm}^{-1}$) ferric wheels and Fe^{III} dinuclear complexes.^{30–34}

To understand the electronic factors that rule the magnetic exchange couplings in these compounds, we have performed DFT calculations on the series of models shown in Figure 5. To avoid expensive and time-consuming calculations, the bridging ligands have been simplified. These series of models allow us to study how the simplification of the bridging ligands can affect the magnitude of the magnetic interaction. These models have been built from the crystallographic structure of **2**. For models **1a**, **2a**, and **3a**, the metal ion and the bridging ligands have been fixed in their experimental geometrical positions, while the peripheral ligands have been substituted by ammonia groups and the nitrogen–metal distances have been optimized, fixing the bond direction. The optimization of the Fe–N bond distances allows a proper tuning of the ligand field of the ammonia group. Models in

(27) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.

(28) Cano, J.; Journaux, Y. Monte Carlo Simulation: A Tool to Analyse the Magnetic Properties. In *Magnetism: Molecules to Materials*; Drillon, M., Ed.; Wiley–VCH: 2004; Vol. 5 (in press).

(29) Wolfram, S. *Mathematica*, version 5.0.

(30) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823.

(31) Raptopoulou, C. P.; Tangoulis, V.; Devlin, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 2386.

(32) Abu-Nawwas, A. H.; Cano, J.; Christian, P.; Mallah, T.; Rajaraman, G.; Teat, S. J.; Winpenny, R. E. P.; Yukawa, Y. *Chem. Commun.* **2004**, 314.

(33) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774.

(34) Scarpellini, M.; Neves, A.; Bortoluzzi, A. J.; Vencato, I. H.; Drago, V.; Ortiz, W. A.; Zucco, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2616.

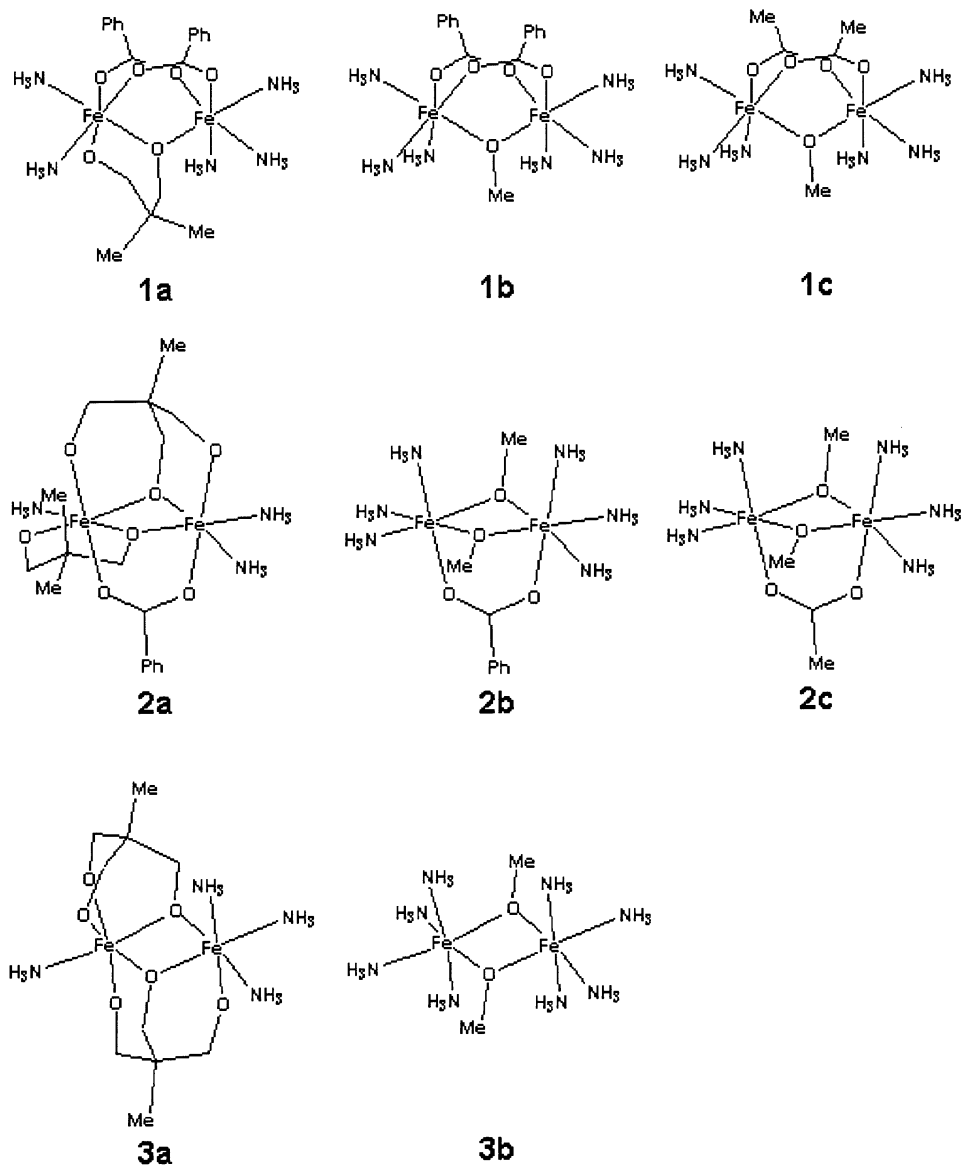


Figure 5. Structure of the models of the three families (1, 2, and 3) corresponding to the three different basic interaction units present in Fe_{16} .

Table 1. Calculated J Values for the Studied Models

	1a	1b	1c	2a	2b	2c	3a	3b	4	5	6	7
J^a	-18.1	-13.3	-23.5	-13.1	-1.5	+1.3	-65.3	-15.9	-0.6	-21.7	-15.3	-32.1
J^b		-25.0		-11.7			-69.3					

^a In reciprocal centimeters. ^b Experimental values for Fe_{16} .

Figure 5 have been grouped into families, representing the three different BIU. In some models, the alkoxide and benzoate ligands have been replaced by simpler methoxide and acetate groups, respectively.

The calculated J values for the studied models are shown in Table 1, together with the experimental J values for **2**. First of all, it can be seen that there is good agreement between the calculated values of the J constants for models **1a**, **2a**, and **3a** and the experimental values of J_1 , J_2 , and J_3 . This agreement confirms the previous assignments of the J_i experimental values. On the other hand, there is a non-negligible change in the J value when the benzoate group is replaced by an acetate ligand (see J values for **1b** and **1c**).

This can be explained since the energies of the orbitals of the benzoate and acetate groups involved in the transmission of the magnetic interaction are different, and consequently, the magnitudes of their interaction with the magnetic orbitals of the metal ions are also different. However, there is another possibility. The methyl group has a weaker electrophilic character than the phenyl group, and so the electronic density on the OCO exchange pathway in the acetate ligand is higher than in the benzoate ligand. This therefore involves a stronger interaction with the magnetic orbitals of the metal ion, a larger energy gap between the SOMOs (single occupied molecular orbitals) and, in line with the Hay–Thibault–Hoffmann (HTH) model,³⁵ a stronger antiferromagnetic

contribution. This has been seen previously in a theoretical study on carboxylate-bridged dinuclear Cu^{II} complexes.³⁶

Neves et al.³⁷ observed that the magnitude of the antiferromagnetic interaction in dinuclear bis(μ -alkoxo) Fe^{III} complexes is rather variable (from -4.4 to -57.2 cm^{-1}) but did not find any correlation between the exchange coupling constants and the structural parameters considered (Fe–O–Fe angles and Fe–Fe distances). From the experimental data in the literature, we have observed that (Table S3), in the same way as the Ruiz studies of dinuclear bis(μ -hydroxo) and bis(μ -alkoxo) Cu^{II} complexes,^{38,39} the magnitude of the interaction depends on the angle formed between the C–O bond in the alkoxo group and the Fe_2O_2 plane, τ , that ranges from 136° to 180° . The antiferromagnetic contribution is stronger when τ is equal to 180° , i.e., when the CO^- group of alkoxo bridging ligand is placed in the same plane as the Fe_2O_2 motif. The average value of τ in model **3a** (153°) is not high enough to explain the strong exchange coupling found in BIU3 (J_3). Another remarkable point is the strong decrease of the magnetic interaction following the substitution of the polyalkoxide ligand by a simpler methoxide group (see J values for models **3a** and **3b**). We have verified that these particular results are not due to an error in the evaluation of the J constant by DFT calculations on these types of systems: we have evaluated the J constant in the experimental compounds $[\text{Fe}_2(\text{heidi})_2(\text{H}_2\text{O})_2]$ and $[\text{Fe}_2(\text{acac})_4(\text{OEt})_2]$ (where H_3heidi and $\text{acac} = [\text{N}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{OH})]$ and pentane-2,4-dionate, respectively),^{40,41} and the calculated values (-21.6 and -22.6 cm^{-1} , respectively) agree with the experimental ones (-26.8 and -22.0 cm^{-1}).

There are three possible reasons to justify the decrease of the exchange coupling from models **3a** to **3b**: (1) the long OCCCO exchange pathway is efficient in the transmission of the magnetic interaction in model **3a**; (2) there is an important peripheral ligand influence, as has been reported for some systems,⁴² due to the substitution of the alkoxide ligands by ammonia groups; or (3) the different electrophilic character of the substituent in the alkoxo group. A tetranuclear Fe^{III} compound of formula $[\text{Fe}_4(\text{thme})_2(\text{C}_3\text{H}_7\text{OH})_6\text{Cl}_6]$ made by us,⁴³ and a complex of formula $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ ⁴⁴ both contain similar metal–oxygen cores in which the central

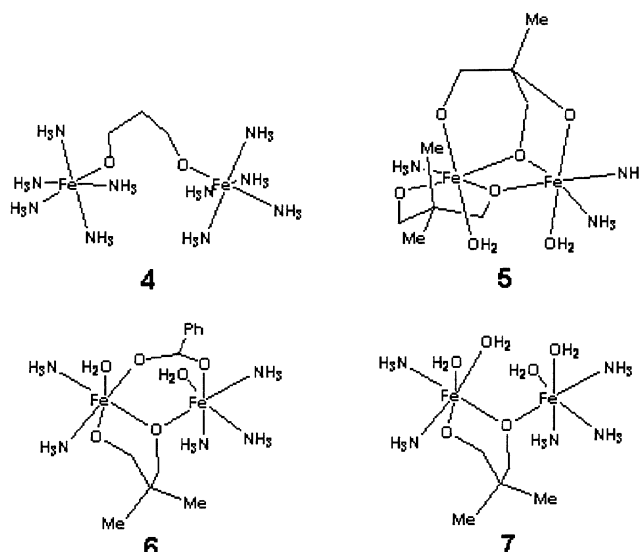


Figure 6. Structure of models 4–7.

metal ion is attached to three peripheral Fe ions arranged in a centered triangle. However, only our compound, $[\text{Fe}_4(\text{thme})_2(\text{C}_3\text{H}_7\text{OH})_6\text{Cl}_6]$, presents the OCCCO exchange pathway thanks to the polyalkoxide ligand that bridges the metal ions. Since both systems show similar Fe–O–Fe angles and exhibit similar antiferromagnetic interactions, we can conclude that the large OCCCO pathway is not efficient for the transmission of the magnetic interaction. Consequently, the polyalkoxide ligand transmits the magnetic interaction through an exchange pathway consisting of only an oxygen atom. Furthermore, the efficiency of the OCCCO pathway has been tested on model **4** (Figure 6), which has been built avoiding steric effects. The obtained J value is -0.6 cm^{-1} . This value confirms the inefficiency of this pathway and validates the chosen interaction topology for **2**, where the interactions between nearest non-neighbors have been neglected. The effect of the peripheral ligand is not large enough to explain the strong decrease of $|J_3|$ values from models **3a** to **3b** and cannot explain the J_3 value obtained from the experimental data. From tabulated Hammett parameters, we can deduce that an alcohol substituent presents a weaker electrophilic character than a methyl group. This electrophilic character decreases even more in the basic (alkoxo) form of the substituent, and a stronger antiferromagnetic interaction can be expected from the thme^{3-} ligand than from the acetate ligand. This would explain the J values found for models **3a** and **3b**. The high experimental $|J_3|$ value obtained here can therefore be explained in the same way. The small deviations in the DFT results from the experimental values for models **1a**, **2a**, and **3a** can be explained by replacement of the peripheral ligands with ammonia molecules.

Finally, in model **3a**, the antiferromagnetic interaction is stronger than in model **2a**. A similar situation is found when model **2b** or **2c** is compared with model **3b**. For model **2b**, even a ferromagnetic interaction is found. Surprisingly, this means that an additional bridging ligand (syn–syn carboxylate ligand) decreases the antiferromagnetic interaction. The butterfly distortion observed in the Fe_2O_2 core cannot account

(35) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(36) Rodríguez-Forteza, A.; Alemany, P.; Alvarez, S.; Ruiz, E. *Chem. Eur. J.* **2001**, *7*, 627.

(37) Neves, A.; Rossi, L. M.; Vencato, I. H.; Haase, W.; Werner, R. *J. Chem. Soc., Dalton Trans.* **2000**, 707 and references therein.

(38) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.

(39) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683.

(40) 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.

(41) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1984**, *23*, 3398.

(42) Román, P.; Guzmán-Miralles, C.; Luque, A.; Beltia, J. L.; Cano, J.; Lloret, F.; Julve, M.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 2858.

(43) Moragues-Cánovas, M.; Collison, D.; Jones, L. F.; Piligkos, S.; Rivière, É.; Ricard, L.; Paulsen, C.; Wernsdorfer, W.; Brechin, E. K.; Mallah, T. *Adv. Mater.* **2004** (in press).

(44) Barra, A. L.; Caneschi, A.; Cornia, A.; Fabrizi de Biani, F.; Gatteschi, D.; Sangregorio, C.; Sessoli, R.; Sorace, L. *J. Am. Chem. Soc.* **1999**, *121*, 5302.

for these results. It is well-known that syn–syn carboxylate and alkoxide bridging ligands that usually transmit antiferromagnetic interactions can, when present simultaneously in some Cu^{II} systems, give rise to the orbital counter-complementarity phenomena, weakening the antiferromagnetic contribution.⁴⁵ In other words, two different bridging ligands can interact with the magnetic orbitals in the metal ions in a different way, destabilizing the in-phase combination in one case and the out-of-phase in the other. So, in systems with two bridging ligands, there is a counterbalance and a compensation of their effects in the formation of the SOMOs. This leads to a decrease in the energy gap between the SOMOs, and therefore a reduction in the antiferromagnetic contributions of each bridge, that can almost cancel each other out, such that the ferromagnetic term dominates. To verify this hypothesis, we have performed DFT calculations on models **5**, **6**, and **7**, shown in Figure 6. These models have been built from the optimized models **1a** and **2a**, where the carboxylate ligands have been replaced by water molecules. The results are shown in Table 1. The antiferromagnetic interaction decreases from model **5** to model **2a**, as expected for an orbital counter-complementarity situation. A similar decrease is observed from model **7** to model **6** or **1a**. It must be pointed out that a relevant orbital counter-complementarity effect is only observed when e_g magnetic orbitals (especially $x^2 - y^2$) are involved. Thus, in the last series of models (**7**, **6**, and **1a**) it is quite difficult to perform a detailed analysis of this effect since this series involves a large number of changes. Despite this, we can draw some conclusions. When two different kinds of bridging ligands are present (**1a**, **2a**, and **6**), the antiferromagnetic interaction is weaker than in the case when there is only one kind of bridging ligand (**3a** and **7**). In this way, from model **7** to model **6**, a decrease of the magnetic interaction is observed. However, there is no significant change in the value of the J constant from model **6** to model **1a**. This may be due to the fact that, since the $x^2 - y^2$ magnetic orbital can only point to the donor atoms of two bridging ligands, the additional carboxylate ligand has no contribution to the counter-complementarity phenomena. Nevertheless, although the e_g orbitals are the main contributors to the magnetic interaction, the t_{2g} orbitals do contribute as well, so a full and detailed analysis of the magnetic interaction is very complicated.

The magnetic properties of polynuclear Fe^{III} complexes containing oxo, hydroxo, alkoxo, and/or carboxylate bridging ligands have been extensively studied in recent years. Whenever possible, exchange couplings are obtained from χT or χ vs T experimental curves. For this purpose, exact or

approximate solutions of partition functions are used.^{28,32,46–50} However, this can be an arduous task in big systems. Some systems present several exchange coupling constants where many sets of parameters are possible, and in general, there is no way to resolve these solutions in any meaningful way. In these cases, a preliminary estimate of the J constants from the electronic structure of the system (or small fragments of it) is a very useful way to search for the correct set of parameters. We have shown in previous work the efficiency of this procedure to study magnetic properties.^{51–53} In our method we evaluate exchange constants from DFT calculations. Weihe and Gudel,⁵⁴ on the other hand, use a different method for the same purpose, and the results obtained from both methods are good. Although the latter method is more intuitive from a classical point of view, it is less useful in quantitative analysis and predictions since (1) it only considers a small set of molecular orbitals, (2) some energies are parametrized and calculated from the qualitative AOM, and (3) some parameters are fitted in order to reproduce the physical properties found in known complexes.

Conclusions

The theoretical evaluation of the exchange coupling constants present in structurally related Fe₈ and Fe₁₆ wheels is in excellent agreement with the experimentally observed data. Calculations show that the exchange is dominated by antiferromagnetic coupling in dinuclear metal units bridged by a combination of alkoxide and carboxylate ligands. The exchange coupling constants decrease when two types of bridging ligands are present, as expected for an orbital counter-complementarity effect.

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Supporting Information Available: Additional calculation details and tables (in PDF format). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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(45) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borrás, J.; Castiñeiras, A. *Eur. J. Inorg. Chem.* **2002**, 8, 2094 and references therein.

- (46) Christmas, C. A.; Tsai, H.; Pardi, L.; Kesselman, J. M.; Gantzel, P. K.; Chadha, R. K.; Gatteschi, D.; Harvey, D. F.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 12483.
 (47) Barra, A. L.; Gatteschi, D.; Sessoli, R. *Chem. Eur. J.* **2000**, *6*, 1608.
 (48) Delfs, C.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Wieghardt, K.; Hanke, D. *Inorg. Chem.* **1993**, *32*, 3099.
 (49) Raha, C.; Rudra, I.; Sen, D.; Ramesha, S. *Phys. Rev B* **2001**, *64*, 064419.
 (50) Benelli, C.; Cano, J.; Journaux, Y.; Sessoli, R.; Solan, G. A.; Winpenny, R. E. P. *Inorg. Chem.* **2001**, *40*, 188.
 (51) Ruiz, E.; Cano, J.; Alvarez, S. *J. Am. Chem. Soc.* (submitted for publication).
 (52) Rajaraman, G.; Cano, J.; Brechin, E. K.; McInnes, E. J. L. *Chem. Commun.* **2004**, 1476.
 (53) Ruiz, E.; Rodriguez-Fortea, A.; Cano, J.; Alvarez, S. *J. Phys. Chem. Solids* **2004**, *65*, 799.
 (54) Weihe, H.; Gudel, H. A. *J. Am. Chem. Soc.* **1998**, *120*, 2870.