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DFT broken-symmetry exchange couplings calculation in a 1D chain of bridged iron basic carboxylates

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ABSTRACT

DFT broken-symmetry calculations at the B3LYP level were carried out to evaluate the exchange coupling constants defined by the Heisenberg–Dirac–van Vleck spin Hamiltonian (HDvV), $\hat{H} = -2J\hat{S}_a\hat{S}_b$, in a 1D chain of iron basic carboxylate cores $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{H}_2\text{O})]$ bridged by dicyanamide, and two related trinuclear Fe_3O moieties. The chain complex was modeled as two Fe_3O units that preserve all features of the repetitive unit in the infinite real system. All geometries were taken from the crystallographic data previously reported. The obtained calculated values for the J constants are in good agreement with experimental results. The weak anti-ferromagnetic inter- Fe_3O core interaction along the chain is also reasonably accounted by the calculations. This methodology appears as a useful tool in the theoretical evaluation of exchange coupling constants in 1D systems.

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1. Introduction

During the last years multinuclear transition metal complexes have been attracting much attention because of their varying magnetic properties among other interesting features [1–6]. Molecular magnetic properties of complexes bearing high spin ground states and negative zero-field splitting values are of vital importance for single-molecule magnets (SMMs) [6]. Usually, their spins are highly exchange-coupled. In these systems the exchange coupling constant, J , of the Heisenberg–Dirac–van Vleck spin Hamiltonian (HDvV), $\hat{H} = -2J\hat{S}_a\hat{S}_b$, which is the most commonly used formalism to interpret the experimental magnetic data, may be computed using the broken symmetry (BS) approach developed by Noodleman et al. as already described in the literature [7,8]. Density functional theory (DFT) has been widely applied to compute the magnetic properties of binuclear transition-metal complexes, organic biradicals, and several organic-radical–transition-metal complexes [9–18] because of the small CPU cost/accuracy ratio achieved by this formalism, allowing one to handle systems of chemical complexity.

The broken symmetry approach within DFT methods has been applied with reasonable success to a big number of dinuclear complexes [9,10] but also to high nuclearity systems [19–21], for which this type of calculations has become more crucial as solving the full Hamiltonian problem for large clusters is not viable due to rapid increase of spin basis set matrix dimensions precluding the energy

levels calculation. Most of the efforts have been performed with discrete molecular systems comprising different number of metallic centers while DFT BS calculations of 1D infinite systems are comparatively still scarce [22–24].

We have recently reported the preparation of a 1D chain complex based on the stringing of an iron basic carboxylate of formula $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{H}_2\text{O})]^+$ (Piv = trimethylacetate) with the bridging dicyanamide anion (dca) [25]. Its crystal structure proves that the chains are well isolated from each other. Magnetic measurements of this complex showed that the individual Fe_3O cores are weakly anti-ferromagnetically coupled through the dca ($J \sim -0.6 \text{ cm}^{-1}$) while strongly anti-ferromagnetically coupled within their own core to afford a well isolated $S = 1/2$ ground state. To give a theoretical support for these experimental results we are reporting in this work DFT broken-symmetry calculations modeling the infinite chain complex as a $\text{Fe}_3\text{O}-\mu\text{-dca}-\text{Fe}_3\text{O}$ dimer. Additionally we are reporting the calculations with the related non-bridged complex $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{CH}_3\text{OH})_2\text{dca}]$ also recently reported by us. Most of the calculations relied in the B3LYP–LanL2DZ hybrid functional-basis set combination that we have successfully employed in the prediction of exchange coupling parameters in a related system [26].

2. Methodology

2.1. Molecular models

For the calculations of the infinite 1D chain complex (**1**) we adopted a discrete model consisting of only a pair of Fe_3O cores bridged by dicyanamide (Fig. 1), which was taken directly, from the X-ray structure [25]. In order to preserve the neutral character

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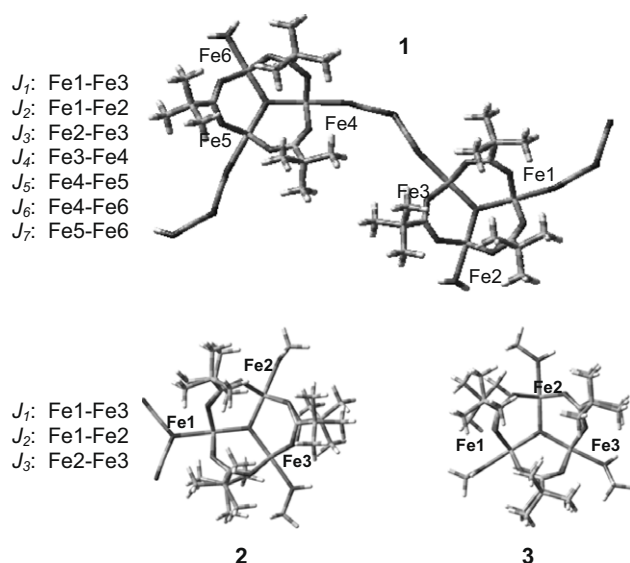


Fig. 1. Structures **1**, **2** and **3** employed in all calculations with the corresponding exchange coupling patterns adopted.

Table 1

Spin topologies describing all calculated broken symmetry states. + and – signs mean spin up and spin down, respectively.

Complex	BS	Fe ₁	Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆
1	1	–	+	+	+	+	+
	2	+	–	+	+	+	+
	3	+	+	–	+	+	+
	4	+	+	+	–	+	+
	5	+	+	+	+	–	+
	6	+	+	+	+	+	–
	7	+	+	–	–	+	+
	8	+	+	+	–	–	–
2	1	–	+	+			
	2	+	–	+			
	3	+	+	–			
3	1	–	+	+			
	2	+	–	+			
	3	+	+	–			

of the real 1D chain, a proton was added to one terminal dca ligand. This hydrogen atom was placed at an ideal position and optimized with a simple molecular mechanics force field. In the case of the non-bridged Fe₃O complexes, the X-ray geometry was employed, running separately calculations for the two species co-crystallized

in the structure [25], [Fe₃O(Piv)₆(CH₃OH)₂dca] (**2**) and [Fe₃O(-Piv)₆(CH₃OH)₃]⁺ (**3**) (Fig. 1).

2.2. DFT calculations

Density functional theory (DFT) spin-unrestricted calculations were performed using the GAUSSIAN03 program [27] (revision D.01) at the B3LYP level employing the *LanL2DZ* basis set and in the case of the smaller complexes **2** and **3** the triple ζ valence split basis set from Ahlrichs with polarization functions (TZVP) was also used. Both basis sets were used as implemented in the Gaussian package. Tightly converged (10^{-8} Eh in energy) single point calculations were performed in order to analyze the exchange coupling between the iron centers. The methodology applied here relies on the broken symmetry formalism, originally developed by Noodleman for SCF methods [7], which involves a variational treatment within the restrictions of a single spin-unrestricted Slater determinant built upon using different orbitals for different spin. This approach has been later applied within the frame of DFT [8]. The HS (high spin) and BS (broken-symmetry) energies were then combined to estimate the exchange coupling parameter J involved in the widespread used Heisenberg–Dirac–van Vleck Hamiltonian:

$$\hat{H}_{\text{HDvV}} = -2J\hat{S}_A\hat{S}_B \quad (1)$$

In the case of complexes **2** and **3**, we have calculated the three possible spin topologies of broken symmetry nature while in the case of the model complex **1** we have calculated seven broken-symmetry states (Table 1). The exchange coupling constants J_i can be obtained after considering the individual pair-like components spin interactions involved in the description of the different broken symmetry states. Three main reported methodologies can be followed: the Ising approach [28], where the broken symmetry states are directly considered as eigenstates of the HDvV Hamiltonian (Eq. (1)) with the corresponding equation:

$$E_{\text{BS}} - E_{\text{HS}} = 2J_{12}(2S_1S_2) \quad (2)$$

the non-projected method proposed by Ruiz and co-workers [19], where the following equation is applied:

$$E_{\text{BS}} - E_{\text{HS}} = 2J_{12}(2S_1S_2 + S_1), \quad \text{with } S_2 < S_1 \quad (3)$$

and finally the generalized multi-spin Yamaguchi method [21], based in the equation:

$$E_{\text{BS}} - E_{\text{HS}} = 2J_{12}(\langle S_1S_2 \rangle_F - \langle S_1S_2 \rangle_{AF}) \quad (4)$$

where $\langle S_1S_2 \rangle$ (F = ferromagnetic, AF = anti-ferromagnetic) are the spin correlation functions between the interacting spins.

In all cases a set of linear equations must be solved to obtain the J parameters.

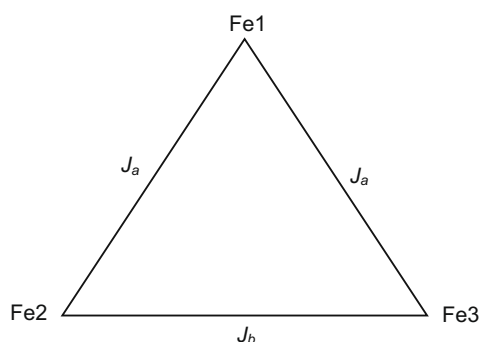
Table 2

Calculated exchange coupling constants for complexes **1**, **2** and **3**. All values in cm^{−1}.

Complex	Method	J1	J2	J3	J4	J5	J6	J7	Exp. ^a
1 ^b	Ruiz	−21.5	−36.2	−38.0	−0.07	−24.4	−35.7	−37.4	$J_a = -35.3$ $J_b = -28.3$ $J' = -0.6$
	Yamaguchi	−25.8	−43.4	−45.4	−0.08	−29.2	−42.7	−44.8	
	Ising	−25.8	−43.5	−45.6	−0.08	−29.3	−42.8	−44.9	
	<i>LanL2DZ</i>				<i>TZVP</i>				
		J1	J2	J3		J1	J2	J3	
2	Ruiz	−32.7	−37.4	−32.8		−35.3	−38.3	−35.3	$J_a = -30.7$ $J_b = -25.5$ or $J_a = -27.0$ $J_b = -33.6$
	Yamaguchi	−39.1	−44.7	−39.3		−42.3	−45.8	−42.3	
	Ising	−39.2	−44.8	−39.4		−42.4	−46.0	−42.4	
3	Ruiz	−36.5	−31.2	−35.4		−38.3	−33.7	−37.4	
	Yamaguchi	−43.7	−38.2	−42.3		−45.9	−40.4	−44.7	
	Ising	−43.8	−38.3	−42.5		−46.0	−40.5	−44.9	

^a From Ref. [25]

^b All with *LanL2DZ* basis set.



Scheme 1. Exchange coupling pattern in the triangular core Fe_3O .

Further details about these methodologies can be found in Ref. [28,19,21].

Additionally, we have also employed the BS-type spin unrestricted solutions after a corresponding orbital transformation (COT) to visualize the interacting non-orthogonal magnetic orbitals [29]. These orbitals do not have a well-defined orbital energy, for this reason, orbital energies are not given explicitly but just their overlapping magnitudes as well as the spin-coupling exchange pathways.

Table 3
Crystallographic $\text{Fe}-\mu_3\text{-O}$ distances in the Fe_3O cores studied.

Complex	Distance/ \AA^a	
1	$\text{Fe}_2\text{-O}, \text{Fe}_6\text{-O}$	1.875
	$\text{Fe}_1\text{-O}, \text{Fe}_5\text{-O}$	1.918
	$\text{Fe}_3\text{-O}, \text{Fe}_4\text{-O}$	1.922
2	$\text{Fe}_1\text{-O}$	1.895
	$\text{Fe}_2\text{-O}$	1.899
	$\text{Fe}_3\text{-O}$	1.914
3	$\text{Fe}_1\text{-O}$	1.907
	$\text{Fe}_2\text{-O}$	1.909
	$\text{Fe}_3\text{-O}$	1.890

^a From Ref. [25].

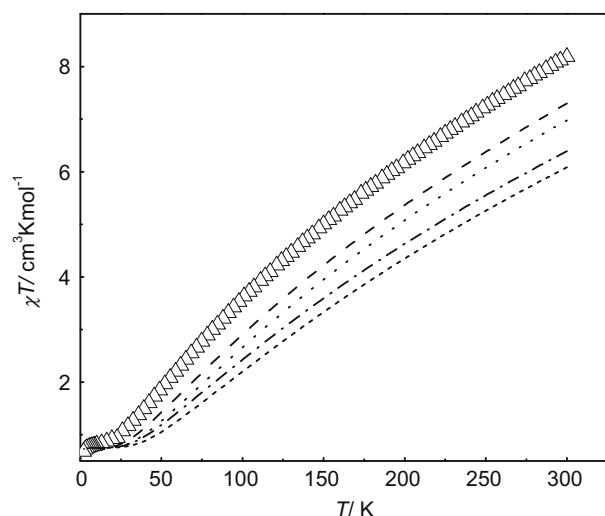


Fig. 2. χT vs. T plot for the complex $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{CH}_3\text{OH})_2\text{dca}].[\text{Fe}_3\text{O}(\text{Piv})_6(\text{CH}_3\text{OH})_3]\text{dca}$. (Δ) Experimental data (Ref. [25]); (—) Ruiz method (LanL2DZ); (...) Ruiz method (TZVP); (---) Yamaguchi method (LanL2DZ); (— · —) Yamaguchi method (TZVP).

3. Results and discussion

3.1. Trinuclear Fe_3O complexes **2** and **3**

The calculated J values for the Fe_3O units in complexes **2** and **3** (Table 2) are in good agreement with the experimental ones [25]. As expected, two J values are essentially identical reproducing the usual $2J$ behavior experimentally observed for this type of triangular Fe_3O cores with three high spin ($S = 5/2$) $\text{Fe}(\text{III})$ ions, and ruled by the following HDvV Hamiltonian (Scheme 1):

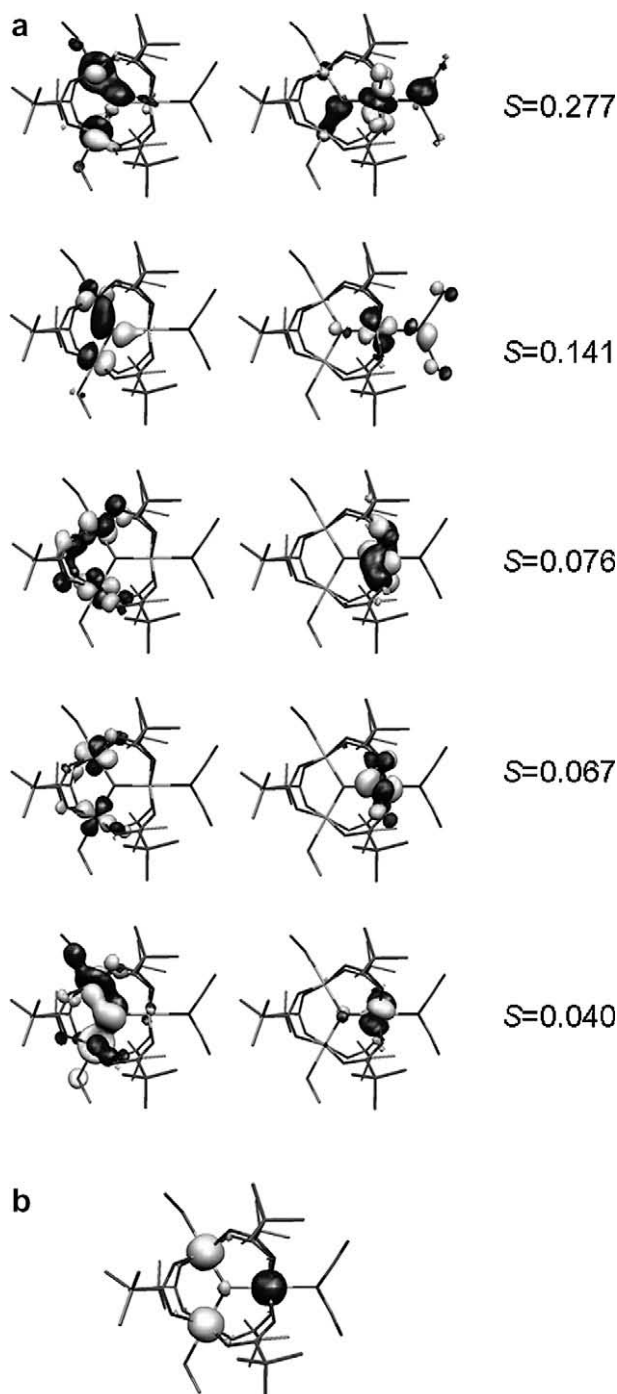


Fig. 3. (a) Magnetic orbitals arising from BS1 after a COT of complex **2** with their corresponding overlaps (S). Left: alpha orbitals, right: beta orbitals. (b) Spin density of BS1 of complex **2**, clear and dark regions corresponds to positive and negative spin densities.

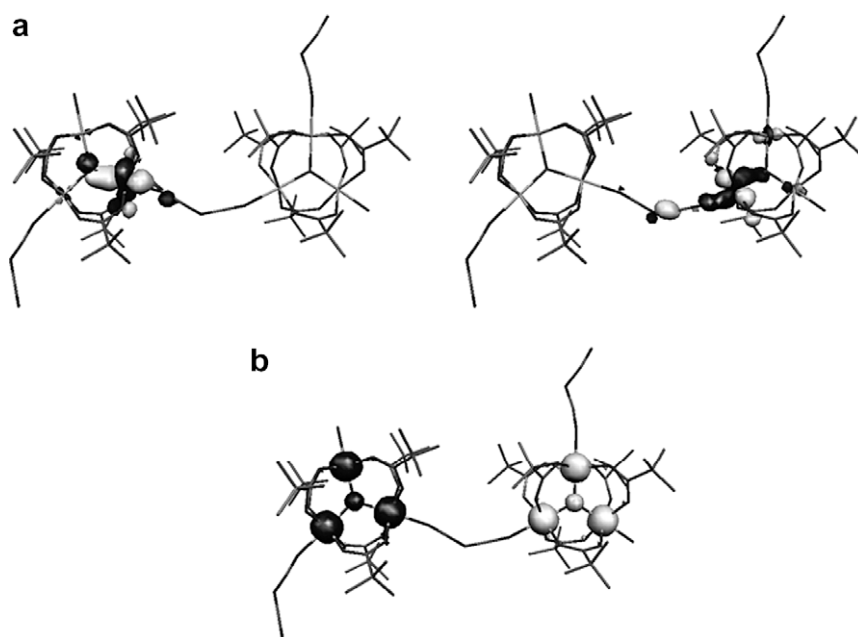


Fig. 4. (a) Magnetic orbitals of complex **1** arising from BS8 after a COT, with a non-negligible overlap trough the dca bridge. Left: alpha orbital, right: beta orbital. (b) Spin density of BS8 of complex **1**, clear and dark regions corresponds to positive and negative spin densities.

$$\hat{H} = -2J_a(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3) - 2J_b(\hat{S}_2 \cdot \hat{S}_3) \quad (5)$$

In the case of complex **2**, the lower obtained $|J|$ value corresponds to J_a , while in complex **3** it corresponds to J_b . This is compatible with experimental data as one short and two long Fe–O–Fe pathways are observed for **2** while the inverse pattern applies in the case of complex **3** (Table 3). It can be noticed that the use of a bigger basis set as TZVP instead of the core effective potential type *LanL2DZ* basis sets does not show an improvement in the final calculated values. It appears also that Ruiz methodology gives the more accurate results while the multi-spin Yamaguchi approach does not represent an improvement with respect to the Ising approximation. The $J_{>}/J_{<}$ ratio is well reproduced with the three methodologies, most noticeably in the case of the *LanL2DZ* basis set, with values of 1.14/1.16, in comparison to the experimental observed of $J_{>}/J_{<} = 1.2$. Hence, the $S = 1/2$ ground state experimentally observed is also reproduced by the calculations. Calculated χT versus T plots,¹ as the 1:1 contribution from complex **2** and **3**, are shown in Fig. 2. It is stressed that an almost identical plot is obtained when using averaged J values for both complexes and a factor of two is applied to the χT plot. This seems to be the most appropriate method as the former cannot be contrasted with experimental values because of severe over-parameterization. From the magnetic orbitals obtained after a COT, it can be observed that the exchange interactions occurred mainly through the central oxo bridging ligand, with two strongly σ -type overlapped magnetic orbitals, while the remaining ones, exhibit a considerably lower overlap, mediated by acetate ligands (Fig. 3). This characteristic is also found when analyzing the magnetic orbitals from the remaining BS states, but in these cases with three oxo mediated strongly overlapped set ($S = 0.258, 0.243$ and 0.153) instead of two. This difference between two or three strongly overlapped magnetic orbitals observed, depending on the spin topology of the BS state, reveals the existence of two different strength exchange interactions within the Fe_3O core, which nicely agrees with the $2J$ model employed.

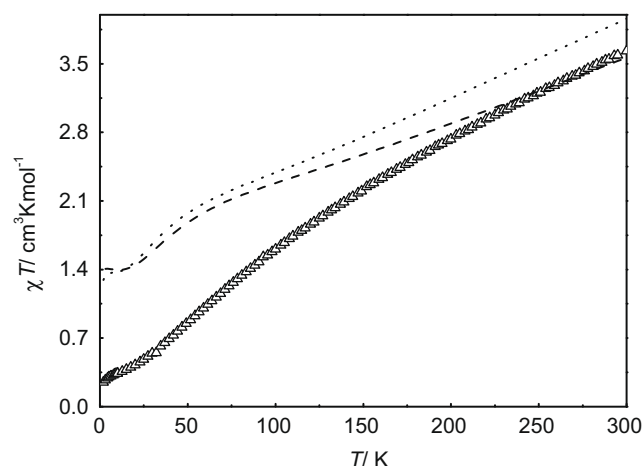


Fig. 5. χT vs. T plot for the model complex **1**. (Δ) Experimental data of the real 1D chain (Ref. [25]); (...) Ruiz method (*LanL2DZ*); (– –) Yamaguchi method (*LanL2DZ*).

3.2. Fe_3O -dca- Fe_3O dimer complex **1** model

The main task in the calculation with the complex **1** model was to evaluate its ability to reproduce the weak anti-ferromagnetic coupling (of the order of 1 cm^{-1}) between the Fe_3O units along the chain. Relying on the results obtained for the Fe_3O isolated complexes we used only the less computing demanding *LanL2DZ* basis set, as the bigger TZVP basis set did not show a real improvement in the calculated J values of the related complexes **2** and **3**. The calculated value around -0.1 cm^{-1} (Table 2) is far away in terms of the relative error (% Rel. error = $|(J_{\text{calc}} - J_{\text{exp}})| / ((J_{\text{calc}} + J_{\text{exp}})/2)$) with respect to -0.6 cm^{-1} , experimentally observed [25] (extracted employing a mean-field approximation correction, $z'/z = 2$), however, it should be considered quite reasonable as it is in the limit of the computation precision. Noteworthy, direct

¹ For details about calculation of simulated χ values refer to Ref. [25].

calculation of this J constant value from the BS8 energy,² afforded a positive value close to 1 cm^{-1} , clearly contradicting the experimental result. Only if all the other, much stronger J values are included by means of the remaining BS states, the right sign for this weak interaction is predicted. In spite of the ferromagnetic interaction obtained by the direct calculation, inspection of the involved magnetic orbitals after a COT shows that there is at least one small ($S = 0.032$) but non-negligible overlap of σ -nature between the Fe centers through the dca bridge (Fig. 4) providing a path for the anti-ferromagnetic coupling. As in the case of the Fe_3O complexes **2** and **3**, the calculated intra- Fe_3O core exchange interactions constants are in good agreement with the experimental values (Table 2). The almost identical values obtained for the pairs $J_1 - J_5$, $J_2 - J_6$ and $J_3 - J_7$ with the additional matching between the two latter pairs corroborates that the inclusion of the extra proton in our model system does not modify substantially the observed exchange coupling pattern in the real 1D complex. Concerning the method employed, a more accurate value for the $J_1 - J_5$ pair is obtained with the Yamaguchi methodology, while for the remaining J pair values Ruiz method appears more accurate. The bigger ratio J_5/J_4 , due to an increased asymmetry in the $\text{Fe}-\mu_3\text{O}$ bonds length (Table 3), in comparison with the Fe_3O complexes **2** and **3** is also well reproduced. When the mean value between the calculated J constants in both Fe_3O moieties of complex **1** is considered, the $S = 1/2$ ground state of the weakly coupled Fe_3O cores in the 1D chain is correctly reproduced with all methods and basis sets. The simulated χT versus T plots are shown in Fig. 5.

4. Conclusions

We have employed a DFT broken-symmetry approach to calculate the different exchange coupling constants in two basic carboxylate iron complexes, $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{CH}_3\text{OH})_2\text{dca}]$ and $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{CH}_3\text{OH})_3]^+$, respectively, as well as in a 1D chain of dca linked Fe_3O units of formula $[\text{Fe}_3\text{O}(\text{Piv})_6(\text{H}_2\text{O})1,5-\mu\text{-dca}]_n$. The obtained values are in good agreement with experimental quantities and the weak anti-ferromagnetic exchange coupling constant between Fe_3O cores mediated by the dicyanamide ligand is reasonably well reproduced. Also the total ground state spin values are well reproduced by the theory. In order to tackle the problem of an infinite chain calculation we adopted a simplified model consisting of only a pair of Fe_3O units but preserving all the ingredients of the repetitive unit in the polymeric structure including the overall neutral charge. The successful results obtained suggest that this

tool could be a promising methodology for calculating exchange coupling constants in 1D infinite systems at a lower computational cost.

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References

- [1] H. Miyasaka, M. Yamashita, Dalton Trans. (2007) 399.
- [2] J.S. Miller, Dalton Trans. (2006) 2742.
- [3] D. Gatteschi, R. Sessoli, J. Magn. Magn. Mater. 272–276 (2004) 1030.
- [4] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268.
- [5] G. Christou, D. Gatteschi, D.N. Hendrickson, R. Sessoli, MRS Bull. 25 (2000) 66.
- [6] D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, 2006.
- [7] L. Noodleman, J. Chem. Phys. 74 (1981) 5737.
- [8] L. Noodleman, E.J. Baerends, J. Am. Chem. Soc. 106 (1984) 2316.
- [9] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 20 (1999) 1391.
- [10] T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, K. Yamaguchi, Chem. Phys. Lett. 319 (2000) 223.
- [11] A. Rodríguez-Forteza, P. Alemany, S. Alvarez, E. Ruiz, A. Sculler, C. Decroix, V. Marvaud, J. Vaissermann, M. Verdaguer, I. Rosenman, M. Julve, Inorg. Chem. 40 (2001) 5868.
- [12] W.G. Han, T. Lovell, T.Q. Liu, L. Noodleman, Inorg. Chem. 42 (2003) 2751.
- [13] O. Loboda, I. Tunell, B. Minaev, H. Agren, Chem. Phys. 312 (2005) 299.
- [14] K. Chlopek, E. Bothe, F. Neese, T. Weyhermuller, K. Wieghardt, Inorg. Chem. 45 (2006) 6298.
- [15] S. Sinnecker, F. Neese, J. Phys. Chem. A 110 (2006) 12267.
- [16] K. Chlopek, N. Muresan, F. Neese, K. Wieghardt, Chem. Eur. J. 13 (2007) 8391.
- [17] K. Ray, T. Petrenko, K. Wieghardt, F. Neese, Dalton Trans. (2007) 1552.
- [18] Y. Takano, T. Taniguchi, H. Isobe, T. Kubo, Y. Morita, K. Yamamoto, K. Nakasuji, T. Takui, K. Yamaguchi, J. Am. Chem. Soc. 124 (2002) 11122.
- [19] E. Ruiz, A. Rodríguez-Forteza, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 24 (2003) 982.
- [20] A. Bencini, F. Totti, Int. J. Quantum Chem. 101 (2005) 819.
- [21] M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, K. Yamaguchi, Chem. Phys. Lett. 432 (2006) 343.
- [22] L.M. Toma, F.S. Delgado, C. Ruiz-Perez, R. Carrasco, J. Cano, F. Lloret, M. Julve, Dalton Trans. (2004) 2836.
- [23] S. Triki, C.J. Gomez-Garcia, E. Ruiz, J. Sala-Pala, Inorg. Chem. 44 (2005) 5501.
- [24] B. Gillon, A. Goujon, S. Willemin, J. Larionova, C. Desplanches, E. Ruiz, G. Andre, J.A. Stride, C. Guerin, Inorg. Chem. 46 (2007) 1090.
- [25] P. Alborés, E. Rentschler, Inorg. Chem. 47 (2008) 7960.
- [26] P. Alborés, E. Rentschler, Eur. J. Inorg. Chem. (2008) 4004.
- [27] M.J. Frisch et al., GAUSSIAN03, Revision D.1, Gaussian Inc., Pittsburgh PA, 2003.
- [28] D.D. Dai, M.H. Whangbo, J. Chem. Phys. 118 (2003) 29.
- [29] F. Neese, J. Phys. Chem. Solids 65 (2004) 781.

² It can be easily realized that the only contribution to this broken symmetry state comes from J_4 .