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Density functional calculations of a tetradecametallic iron(III) cluster with a very large spin ground state.

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Density functional theory (DFT) calculations and Monte Carlo (MC) simulations are used to calculate the exchange interactions in the Fe(III) cluster [$Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6$], impossible to determine by conventional methods – the results support a huge ground state spin arising from competing antiferromagnetic interactions.

Reliable calculation of magnetic exchange interactions (J) in transition metal clusters using DFT has been demonstrated recently by Alvarez and co-workers.[1] This methodology provides a powerful tool to model magnetic properties of clusters that are too big to treat by conventional matrix diagonalisation methods. Here we apply DFT to the tetradecametallic Fe(III) cluster [$Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6$] (**1**, Fig. 1; Hbta = benzotriazole),[2] where magnetisation measurements show a ground spin state of at least $S = 23$, but possibly as high as $S = 25$. The DFT derived J-values, refined by MC simulations of experimental magnetic data, support a ferrimagnetic spin structure[2] resulting in the very high spin.

The structure of **1** contains two {$Fe_4(bta)_3Cl_3$} fragments sandwiching a central Fe_6 ring *via* 18 μ_2-methoxides and 6 μ_4-oxides (Fig. 1).[2] The metallic skeleton is a hexacapped hexagonal bipyramid, with the caps on alternate faces. This gives four chemically distinct, nearest neighbour Fe···Fe exchange interactions (Fig. 2, considering only single atom bridged pathways, which are expected to be dominant): (i) six J_1 interactions between the apical ion Fe1 (see Fig. 2 for numbering scheme) and each of the face caps Fe2, Fe3 and Fe4, and the symmetry equivalent interactions (the molecule has crystallographic inversion symmetry), *via* μ_4-O bridges with Fe–O–Fe angles 113.0° to 114.2°; (ii) twelve J_2 interactions between the face caps and each of the central Fe_6 ring (Fe2–Fe12, Fe2–Fe13, *etc.*) *via* μ_2-OMe (98.5° to 101.7°) and μ_4-O (95.2° to 96.5°); (iii) twelve J_3 interactions between the apical ions and each of the Fe_6 ring (Fe1–Fe5, Fe1–Fe6, etc) *via* μ_4-O (123.6° to 126.0°); and (iv) six J_4 interactions within the Fe_6 ring (Fe5–Fe6, Fe6–Fe7, *etc.*) *via* μ_2-OMe (100.9° to 101.3°) and μ_4-O (94.5° to 95.3°).

The spin-Hamiltonian is then:

$$\begin{aligned}\hat{H} = -J_1[&\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_8\hat{S}_9 + \hat{S}_8\hat{S}_{10} + \hat{S}_8\hat{S}_{11}]\\ -J_2[&\hat{S}_2\hat{S}_{12} + \hat{S}_2\hat{S}_{13} + \hat{S}_4\hat{S}_6 + \hat{S}_4\hat{S}_7 + \hat{S}_3\hat{S}_5 + \hat{S}_3\hat{S}_{14}]\\ &\hat{S}_{10}\hat{S}_7 + \hat{S}_{10}\hat{S}_{12} + \hat{S}_9\hat{S}_5 + \hat{S}_9\hat{S}_6 + \hat{S}_{11}\hat{S}_{13} + \hat{S}_{11}\hat{S}_{14}]\\ -J_3[&\hat{S}_1\hat{S}_5 + \hat{S}_1\hat{S}_6 + \hat{S}_1\hat{S}_7 + \hat{S}_1\hat{S}_{12} + \hat{S}_1\hat{S}_{13} + \hat{S}_1\hat{S}_{14}]\\ &\hat{S}_8\hat{S}_5 + \hat{S}_8\hat{S}_6 + \hat{S}_8\hat{S}_7 + \hat{S}_8\hat{S}_{12} + \hat{S}_8\hat{S}_{13} + \hat{S}_8\hat{S}_{14}]\\ -J_4[&\hat{S}_5\hat{S}_6 + \hat{S}_5\hat{S}_{14} + \hat{S}_6\hat{S}_7 + \hat{S}_7\hat{S}_{12} + \hat{S}_{12}\hat{S}_{13} + \hat{S}_{13}\hat{S}_{14}]\end{aligned}$$

It is not possible to calculate χT *via* this Hamiltonian with fourteen $S = 5/2$ ions by standard matrix diagonalisation methods. Therefore, an alternative strategy is necessary. In some circumstances MC simulations can be used to determine J-values in clusters.[3] However, for large clusters with many exchange interactions, as is the case with **1**, this can lead to over-parameterisation and unreliable results. Therefore, we have used DFT to calculate the J-values and used these values as a good starting point for the MC simulations of the experimental χT data to refine the solution. DFT calculations were performed on **1** using Siesta 1.3 density functional software and PBE functionals together with DZP basis sets implemented on Siesta.[4] The full crystal structure was used, and single point calculations performed to calculate the energy of the spin configurations.

To derive four J-values, the energies of five different spin configurations need to be calculated – the differences in energies between these five states (STi, i = 1,5) can then be related to the J-values using a pair-wise interaction model.[1] The spin configurations used were: ST1 – all iron ions "spin up"; ST2 – Fe1 and Fe8 spin up, all others spin down (Fig. 2); ST3 – Fe1, Fe2, Fe3, Fe4, Fe8, Fe9, Fe10, Fe11 spin up, all others down; ST4 – Fe1, Fe5, Fe6, Fe7, Fe12, Fe13, Fe14 spin up, all others down; ST5 – Fe1, Fe2, Fe3, Fe4, Fe5, Fe7, Fe8, Fe10, Fe11, Fe13 spin up, all others down. The DFT calculated energies are summarised in Fig. 3. Of the five chosen configurations, ST2 has the lowest calculated energy. The

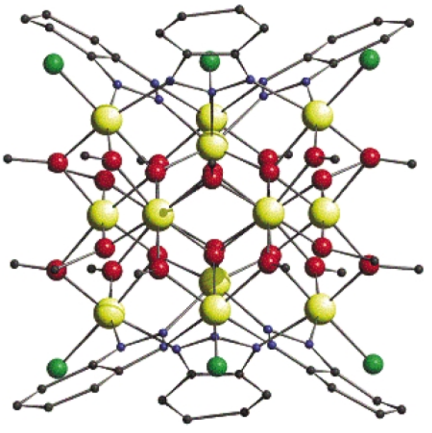

Fig. 1 Structure of **1**: yellow Fe, blue N, green Cl, red O, black C, H atoms omitted for clarity.

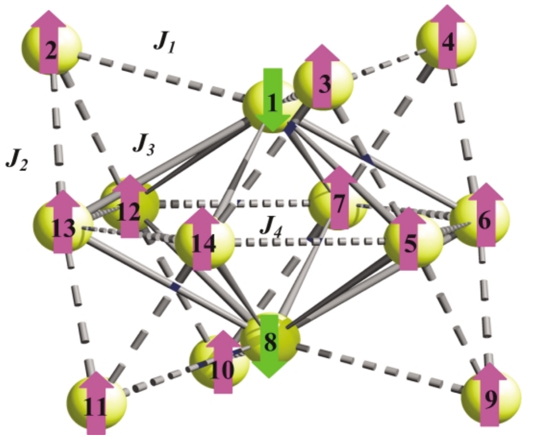

Fig. 2 Metallic core of **1**, highlighting the four chemically distinct exchange interactions. The spin configuration shown corresponds to the most stable of the calculated spin states (ST2).

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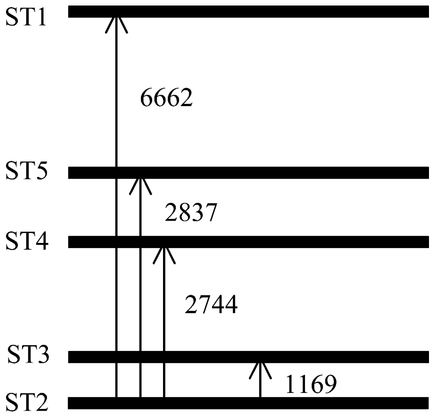

Fig. 3 Relative energies (cm^{-1}) of the spin configurations ST1–ST5 obtained by DFT calculations, where ST2 has been taken as reference.

relationships between the energy differences and the *J*-values are eqns. (1)–(4).

$$\frac{E_{ST1}-E_{ST2}}{15}=6J_1-12J_3 \tag{1}$$

$$\frac{E_{ST1}-E_{ST3}}{15}=12J_2-12J_3 \tag{2}$$

$$\frac{E_{ST1}-E_{ST4}}{15}=6J_1-12J_2 \tag{3}$$

$$\frac{E_{ST1}-E_{ST5}}{15}=6J_2-6J_3-6J_4 \tag{4}$$

With the DFT calculated energies, eqns. (1) to (4) give $J_1 = -22.4$ cm^{-1}, $J_2 = -10.5$ cm^{-1}, $J_3 = -25.8$ cm^{-1}, $J_4 = -6.1$ cm^{-1}. Thus, J_1, J_2, J_3 and J_4 are all antiferromagnetic and the $J_3 < J_1 < J_2 < J_4$ trend is as expected from the Fe–O–Fe angles, where stronger antiferromagnetic coupling is expected for larger angles.[5]

Since it is not possible to solve the Heisenberg spin-Hamiltonian, we have applied MC methods to simulate the χT *vs.* T curve using the DFT calculated *J*-values. MC simulations were performed using the metropolis algorithm. In all simulations we have employed the classical spin approach (classical MC) that can be applied to systems with large local spin moments, as in **1**. In these simulations χ has been calculated from the fluctuations in the magnetization in zero external magnetic field. The number of steps in the MC simulation for each temperature is $5\times10^7/T$ (*T* in K). Thus, we include more steps in the sampling at low *T* because the change of the spin configuration is more difficult at such temperatures. 10% of the steps are employed for thermalisation of the system. To avoid freezing of the spin configuration we "cool down" slower at low *T*. χT is calculated down to 10 K since at low *T* the classical spin approach is less correct due to the energy spectrum not looking like a continuum, especially in systems with a few magnetic sites.

Initially we calculated the χT *vs.* T curve using the *fixed* DFT *J*-values (Fig. 4), and a fixed *g*-value of 2.0. Note that the experimental data below *ca*. 70 K are compromised by intermolecular and/or zero-field splitting effects.[2] Intermolecular effects are likely to be significant even at these relatively high temperatures since *S* is so big (we have recently prepared bulkier derivatives of **1** which show higher maxima in χT). Moreover, even with a small *D* value of *ca*. 0.1 K,[2] the energy spread of an $S = 23$ manifold is > 50 cm^{-1}. Neither of these phenomena are accounted for in our MC calculations. Although the shape of the calculated curve is good using the fixed DFT *J*-values, the absolute values of χT are too low at all temperatures (Fig. 4).

Therefore, the DFT *J*-values were refined by a MC *fitting* procedure in the temperature range 300–70 K (see above). This gives $J_1 = -22.0$ cm^{-1}, $J_2 = -8.7$ cm^{-1}, $J_3 = -29.7$ cm^{-1}, $J_4 = -3.7$ cm^{-1}, and there is now an excellent agreement between the calculated and experimental curves in this *T* range (Fig. 4). Note that the MC fitted values are only perturbed from the DFT values by a very small amount, demonstrating the sensitivity of χT to small changes in *J* and thus providing confidence in the signs, magnitude and relative magnitudes of the *J*-values.

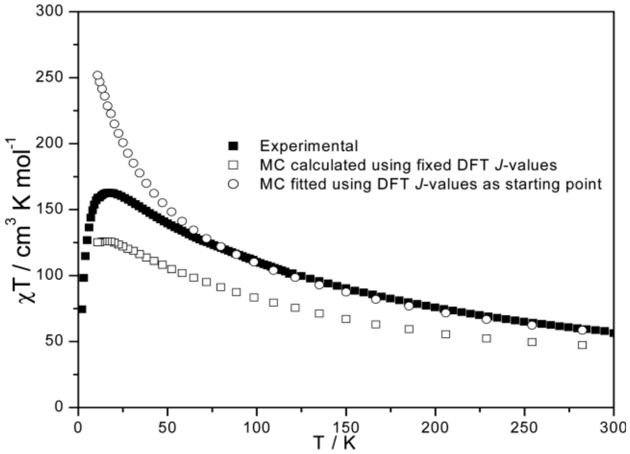

Fig. 4 Experimental and MC calculated χT *vs.* T data for **1**.

The $J_3 < J_1 < J_2 < J_4$ ordering gives the strongest interactions between the apical and equatorial ions (J_3), and the next strongest between the apical and face-cap ions (J_1). If the ratios of J_3/J_2, J_1/J_2 and J_3/J_4 are large enough, then J_3 and J_1 will over-ride the weaker antiferromagnetic interactions between the face-cap and equatorial ions (J_2) and among the equatorial ions (J_4), resulting in a ground state with the spins on the apical ions parallel to each other (say, spin down) but anti-parallel to all the others (spin up). This corresponds to ST2 (Fig. 2) and would give a ground state $S = 25$. However, when there are competing antiferromagnetic exchange interactions subtle changes in ratios of the competing *J*-values can lead to changes in the ground state.[6] We believe that this causes the stark difference between the two calculated curves (Fig. 4). To probe this we performed further MC calculations. Firstly, we fixed the *ratios* of all the *J*-values to those found by DFT and fitted with a single scaling factor – this approach gives poor fits. Secondly, we fixed J_3 and J_1 at their fitted values and varied J_2 systematically about its fitted value (J_2 being more important than the much weaker J_4), thus varying the J_1/J_2 and J_3/J_2 ratios. We find that with ratios above *ca*. 2.3 and 2.7, respectively, good fits to the high temperature χT are found, while below these ratios calculated χT values are too low at all temperatures. Thus we conclude that above these ratios (as in the MC fitted values) a higher spin ground state, consistent with experiment, is found than with lower ratios (as in the DFT values), even though the absolute *J*-values are very close.

In conclusion, DFT calculations in conjunction with MC simulation methods can be used to extract good estimates of the magnetic exchange interactions in transition metal clusters that are too big to derive by traditional methods or even by MC methods alone. The *J*-values determined here are consistent with the very high ground spin state of **1** determined previously by magnetisation measurements.[2]

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