An attempt to understand the observed plateau of the magnetization in tetranuclear iron(II) complexes of thiacalixarene macrocycles

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Abstract. The next-nearest-neighbour (NNN) effect in tetranuclear iron(II) complexes of thiacalixarene macrocycles using the isotropic Heisenberg model has been investigated in order to understand its effects on the observed plateau of magnetization. Although NNN effect is generally very weak in these kinds of systems, it was calculated that its response is quite significant to the external perturbations in certain temperature regions. Using the isotropic Heisenberg exchange Hamiltonian, zero-field energy spectra have been calculated for this particular tetranuclear system. The average magnetic moments with and without next-nearest-neighbour interactions were also calculated. In order to verify the calculations, the results were compared with experimental data taken from the literature, whence, it is suggested that observed magnetic behaviour can be improved by taking into account the NNN effect.

Keywords. Magnetic susceptibility; next-nearest-neighbour effects; tetranuclear Fe(II) complexes; antiferromagnetic exchange; plateau.

PACS Nos 33.15.Kr; 75.10.Jm; 75.30.Et; 71.70.-d; 75.30.Kz

1. Introduction

The magnetic properties of large clusters in which magnetic centres interact with each other have gained much interest among many scientists [1–10]. Molecular clusters of metal ions have been of great interest to both physicists and chemists as they can serve as model systems to investigate exchange interactions. Additionally, many such clusters behave as single-domain magnetic particles which are generally called single molecule magnets. Although many polynuclear complexes have been

isolated, only a few of them act as single molecule magnets at some practically applicable temperature range [11–15]. Among the single molecule magnets, the polynuclear metal complexes of thiacalixarene macrocycles have been studied during the past few years. The structures and magnetic behaviours of many of these complexes are well understood. However, recently, an unexpected magnetic behaviour in a certain temperature range has been observed for tetra and decanuclear iron(II) complexes of thiacalixarene macrocycles [11–15]. The observed plateau in a certain temperature range has not been understood properly yet [15]. There is not much plateau-like magnetic behaviour reported for small clusters in the literature. This study aims to understand this unexpected behaviour. The observed magnetization was simulated by a single exchange coupling between the iron(II) ions by using the isotropic Heisenberg model [15]. But, there is not enough information about a possible discrepancy in the observed behaviour. However, a very small amount of impurities, a next-nearest-neighbour coupling, and various exchange terms derived from complex ion term can be the reasons for the possible effects of such discrepancy [8,9]. In this research, one possible effect, which may cause a discrepancy in the observed behaviour, namely, the next-nearest-neighbour interactions, have been studied for tetranuclear case. The main reason for applying the NNN effect among the above-mentioned effects is that it causes some interesting physical situations such as non-collinearity of spin arrangements bringing frustrations of spin, bearing in mind that its effect is almost negligible in these kinds of spin systems from the magnetism point of view. (Obviously there are many tetranuclear spin clusters in which these effects are much more important, such as the magnitude of NNN that may lead to a frustrated state in those systems [16,17]). It is well known that frustration gives rise to spectacular and often unexpected behaviours at low temperatures due to high degeneracy of the ground state [18–24]. The frustrated phenomena have been studied for a long time both experimentally and theoretically for various systems [16–25]. Another reason is that the calculated magnetization may be improved by introducing some more terms in the spin-Hamiltonian. Another reason is that an intermediate antiferromagnetic spin state in some metal clusters, in which the spin frustration effects contribute to its stabilization, especially at lower temperatures, may exist [26]. This frustration phenomenon occurs when an exchange coupled magnetic ion does not satisfy all of its magnetic bands, and hence does not know what direction to point [27–31]. In a molecular magnet, frustration can arise due to geometrical frustration via competing interactions between magnetic moments having equal magnitude [32–34]. And the final reason is that although there is no clear pathway for NNN interactions via the bridging ligands, small amounts of metal–metal overlapping, which may lead to this interaction in this geometrical entity, is not impossible.

2. Phenomenological Hamiltonian to describe exchange interactions

When dealing with antiferromagnetic systems, the Heisenberg Hamiltonian is perhaps the simplest spin model with a localized spin on each lattice site interacting with its nearest neighbours via an antiferromagnetic coupling as

$$H = -J \sum_{i,j} \vec{S}_i \cdot \vec{S}_j,$$

where J is the isotropic exchange coupling constant and $\vec{S}_i$ and $\vec{S}_j$ are the resultant spins of neighbouring atoms, each of which is the quantum mechanical operator.

Generally the energy spectrum is described by an effective spin-Hamiltonian. Its simplest form, containing interactions among spin centres, ligand field effects and Zeeman splitting is

$$H = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot \vec{D}_i \cdot \vec{S}_i + \mu_{\mathrm{B}} \sum_i \vec{S}_i \cdot \vec{g}_i \cdot \vec{B},$$

where i and j run over all spin centres, $\vec{D}_i$ and $\vec{g}_i$ denote Cartesian tensors [8,9,35–40].

Such a phenomenological description was first introduced by Heisenberg, then discussed by Dirac and Van Vleck. The above equation is generally called Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian.

3. Average magnetic moment and magnetic susceptibility of tetranuclear Fe(II) cluster

Assuming an ideal square spin situation, the appropriate spin-Hamiltonian for the theoretical interpretation can be given as

$$H = -J_1(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_4 + \vec{S}_4 \cdot \vec{S}_1)$$
$$-J_2(\vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_4) + \mu_{\mathrm{B}} g \sum_{i=1}^{4} \vec{S}_i \cdot \vec{B},$$

where H consists of the isotropic nearest and next-nearest-neighbour exchange terms and the Zeeman terms for four metal centres. It is assumed that the dipole–dipole interaction terms and the second-order ligand field terms are negligible such that g_i local Zeeman factors of each centre are equal. J_1 and J_2 indicate the first and the second nearest-neighbour coupling strength respectively. It should be noted here that in order to use the above Hamiltonian, the orbital angular momentum of the term wave function of each Fe(II) ion needs to be zero. The interactions between neighbours are certainly much larger than those between the next-nearest-neighbours which can easily be seen from their interaction pathways as shown in figure 1. The zero-field spin-Hamiltonian can easily be found in the above Hamiltonian. Assuming that all the spins at each side have equal magnitude, the energy spectrum of this Hamiltonian can be derived as

$$E(S, S_A, S_B) = -\frac{J_1}{2} S(S+1) - \frac{J_2}{2} [S_A(S_A + 1) + S_B(S_B + 1)],$$

where

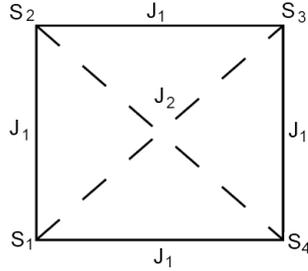$$\vec{S}_A = \vec{S}_1 + \vec{S}_3, \quad \vec{S}_B = \vec{S}_2 + \vec{S}_4$$

Figure 1. Interaction pathways in tetranuclear Fe(II) cluster.

$$\vec{S} = \vec{S}_A + \vec{S}_B.$$

Dividing both sides of this equation by J_1, one may obtain another energy equation as

$$e(S, S_A, S_B) = -\frac{1}{2}S(S+1) - \frac{x}{2}[S_A(S_A+1) + S_B(S_B+1)].$$

From this equation, the zero-field energies as a function of $x = J_2/J_1$ can be easily calculated.

It is important to note that some states with the same value of S may have different energies and thus extra attention must be paid when performing the summation over all states in calculating the average magnetic moment and susceptibility. Once the energy spectrum of isotropic Heisenberg Hamiltonian is found, the magnetic susceptibility can be calculated using the well-known formula of Van Vleck as already given in [8,9,35–40]

$$\chi(T) = \frac{N\beta^2 g^2}{3kT} \frac{\sum_S S(S+1)(2S+1)\exp\left(-\frac{E(S,S_A,S_B)}{kT}\right)}{\sum_S (2S+1)\exp\left(-\frac{E(S,S_A,S_B)}{kT}\right)}$$

and magnetic moment as [8,9,35–40]

$$m(T, B) = N\beta g \frac{\sum_S \sinh\left(\frac{2S+1}{2}y\right) SB_S(Sy)\exp\left(-\frac{E(S,S_A,S_B)}{kT}\right)}{\sum_S \sinh\left(\frac{2S+1}{2}y\right) \exp\left(-\frac{E(S,S_A,S_B)}{kT}\right)},$$

where $y = g\beta B/kT$ and $B_S(S, y)$ is the Brillouin function. Since high-spin six-coordinated Fe(II) ions have four unpaired electrons, taking $S = 2$ and using the particular value of J_1, which is around -4.0 cm^{-1} [15] for the above-mentioned system, and adding a small amount of J_2 (for positive and negative signs), the behaviour of magnetic susceptibility as a function of temperature is shown in figure 2.

4. Results and discussions

There are some interesting results that can be derived from the temperature dependence of the susceptibility in the presence of J_2 such as
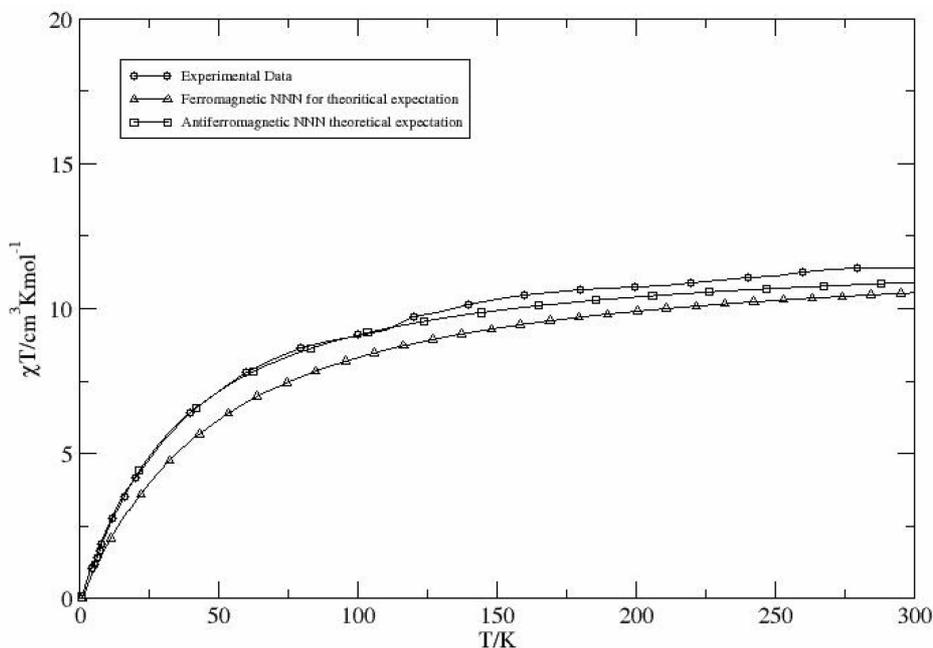
Figure 2. Simulated temperature-dependent susceptibility with NNN.

(1) As might be expected, the average magnetic moment would be reduced in the presence of a very small amount of antiferromagnetic J_2.

(2) As can be seen from figure 2 the ferromagnetic J_2 is not relevant for this system since it produces the worst result.

(3) In spite of the fact that the nature of J_2 is against the ordering (but not complete disorder), it is quite clear from the calculated average magnetic moment with and without next-nearest-neighbour effect that, it behaves as if it is against disordering and helps the antiferromagnetization in the lower temperature range (since it causes a small reduction of magnetic moment in the low-temperature range). But it should be noted that a pronounced reduction began to emerge when J_2 is >10% J_1, which is not likely in this system.

(4) Although the inclusion of NNN may improve the simulation, it does not produce any plateau which is observed in the title system.

As a result, it can be said that even though some of the discrepancies can be obtained by including enough amount of antiferromagnetic J_2 into the spin-Hamiltonian, the observed plateau cannot be obtained with this effect alone. So it is suggested that the issue should be further investigated with other negligible effects in order to be sure about the main reasons behind the observed plateau.

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5. Conclusion

Since in an antiferromagnetic system the nature of NNN effect may cause many interesting physical situations, such as non-collinearity of spin arrangements which also brings frustrations of spin, this effect is applied in tetranuclear Fe(II) complexes of thiacalixarene macrocycle in order to see whether any improvement can be obtained for the observed behaviour. The calculated results showed that by adding a few percentages of second neighbour effects into the isotropic Heisenberg model for the above-mentioned system, some discrepancy from the observed behaviour can be achieved. However, as was noted earlier, in order to get sufficient results the added amount should not be less than 10% J_1 which is not likely in this system. So, it seems that this effect itself does not cause a significant improvement to the magnetization and it does not produce any plateau for the magnetization. It is possible that studying this effect together with other negligible effects may improve the magnetization but any plateau in the susceptibility seems to be quite unlikely for these effects. All the above possibilities suggest that one should question the validity of the isotropic Heisenberg Hamiltonian since six-coordinated Fe(II) ions have $^5T_2$ ground term wave function, which brings some orbital contribution to the magnetic moment and indicates that one should be careful when using the isotropic Heisenberg model. This point is left for a future study.

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