OPTOELECTRONİCS AND ADVANCED MATERİALS – RAPİD COMMUNİCATİONS Vol. 4, No. 5, May 2010, p. 740 – 743

Antiferromagnetic exchange interactions in asymmetrically bridged dinuclear Fe(III) complexes by phenoxo and metoxo groups: magnetic field dependence of magnetisation

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In this study the antiferromagnetic interactions in recently synthesized dinuclear Fe(III) complex has been investigated in a magnetic field. For this purpose the magnetic moment of Fe(III) ions has been calculated in the vicinity of the magnetic field. Using the reported coupling constant, it was shown that the magnetic moment takes a ladder like behavior below a certain temperature. It was also shown that the saturation magnetization can be more easily obtained for small coupling constant.

(Received April 02, 2010; accepted May 20, 2010)

Keywords: Magnetization, Magnetic susceptibility, Antiferromagnetic coupling, Fe(III) dimmer

1. Introduction

There is a growing interest in the study of dinuclear transition metal complexes where several electronic spins are coupled with dominant isotropic exchange integrals [1-15]. An important hindrance for the development of the field of molecular magnetism is the scarcity of bridging ligands that favors antiferromagnetic coupling in di or polynuclear transition metal complexes[6,13-16]. Owing to this, magnetic behaviours of materials based on molecular entities have been extensively explored from experimental and theoretical points of view during the past few decades. The most common magnetic polymers of this type consist of metal ions bridged by organic ligands forming polymeric structures. Such materials consist of truly magnetic molecules, whose magnetic moments are delocalized within the molecular unit, interacting with each other by means of electrostatic forces. The magnetic behavior of several compounds in this class of inorganics and organometallic polymers beautifully illustrates some of the properties of amorphous magnetism [16]. Dinuclear Fe(III) compounds are of particular interest due to their stability in the dimeric form and their magnetic interactions between Fe ions especially in asymmetrically bridged by a phenoxo and methoxo groups where the interactions becomes pronounceable at lower temperatures[13]. Recently synthesis and a proper characterization of a new dinuclear iron(III) complexes asymmetrically bridged by a phenoxo and methoxo groups have been reported. It is quite clear from their work that, there is a pronounceable intramolecular antiferromagnetic interactions between Fe(III) ions. It is apparent in the literature that there is a growing interest to the study of binucleating Schiff base ligands are highly inclined to give homo and hetero polynuclear complexes with many transition metal ions and their complexes [13,17-20]. This is partly because of the interest in relating structures to magnetic exchange effects in homo-and hetero-binuclear metal complexes of those ligands [21,22] and partly because of the use of such complexes to mimic aspects of two metal biosites in various proteins and enzymes [23,24]. These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [25-28]. Especially, dinuclear iron(III) complexes provide structural models for dinuclear sites in several proteins involved in oxygen storage of hemerytherin and oxygen activation of methanemonooxygenase [29-32]. In addition, these systems were treated as model systems for understanding of the size and magnitude of super-exchange coupling interactions in theoretical considerations.There are some quantitative magnetostructural studies for dinuclear iron(III) centers, doubly bridged by oxygen atoms [33]. The influence of the geometrical parameters in Fe_2O_2 bridging systems, the Fe–O bond distances and the Fe–O–Fe bond angles, on the super-exchange integral, however, is not yet understood in detail due to lack of structural data [34-36]. Studies of some iron complexes have shown that the oxo- bridge is responsible for the strong antiferromagnetic coupling (usually $-50 > J > -200$ cm-1) [37-40] and those complexes with alkoxo, phenoxo, or hydroxo- bridges are weakly coupled (usually $0 > J > -30$ cm-1) [40-47]. But, how the exchange coupling constants for dinuclear iron(III) compounds containing the Fe_2O_2 bridging system are influenced by variations in the geometrical and chemical features of the bridging and nonbridging ligands is not yet understood [34-36]. Previously the structures and magnetic properties of several dinuclear iron(III) complexes have been reported

[12,40-44]. It can be seen from the reported study, the exchange coupling constant varies in the interval of -7.5,-11. In this study we mainly concentrated to the magnetic behaviour of dinuclear Fe(III) ions in a magnetic field with using the reported j values. It is already known that if the two centers with nonzero spins are bonded not directly but via intermediate groups, the spin-spin interaction between them becomes more complicated, involving electrons of intermediate centers[6,14,15,48,49]. In such a case the observed magnetic moment may show a big dispersion from the spin only value[6,14,15].

2. Phenomenological Hamiltonian to describe exchange interactions

The main parameter used to quantify the magnetic properties of dinuclear complexes is the exchange coupling constant J between the two paramagnetic centers with total spins S_1 and S_2 respectively, which is defined through the phenomenological Heisenberg Hamiltonian [14,15,48-56]:

$$H = -J\vec{S}_1 \cdot \vec{S}_2$$

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

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

where i and j runs over all spin centers, $\vec{D}_i$ and $\vec{g}_i$ denote Cartesian tensors [14,15,48,54-56].

3. Average magnetic moment and magnetic susceptibility of dimeric Fe^{3+} ions

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

$$H = -J\vec{S}_1 \cdot \vec{S}_2$$

where H consists of the isotropic exchange term. The isotropic interaction phenomenon is purely electrostatic in nature [14,15,47-56]. 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. Since

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

hence

$$\vec{S}^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$$

The Hamiltonian may be rewritten as

$$H = -\frac{J}{2}\left(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2\right)$$

the eigenvalues of which are

$$E(S,S_1,S_2) = -\frac{J}{2}[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$$

$$\chi(T) = \frac{N\beta^2 g^2}{3kT} \frac{\sum_S S(S+1)(2S+1)\exp-\left(\frac{E(S,S_1,S_2)}{kT}\right)}{\sum_S (2S+1)\exp-\left(\frac{E(S,S_1,S_2)}{kT}\right)}$$

and magnetic moment as [14,15,48,54-56]

$$m(T,B) = N\beta g \frac{\sum_S \sinh\left(\frac{2S+1}{2}y\right) SB_S(Sy)\exp\left(-\frac{E(S,S_1,S_2)}{kT}\right)}{\sum_S \sinh\left(\frac{2S+1}{2}y\right)\exp\left(-\frac{E(S,S_1,S_2)}{kT}\right)}$$

where $y = \frac{g\beta B}{kT}$ and $B_S(S,y)$ is the Brillouin function.

Using the reported j values, the magnetic moments of the reported complexes have been drawn from Fig. 1 and Fig. 4

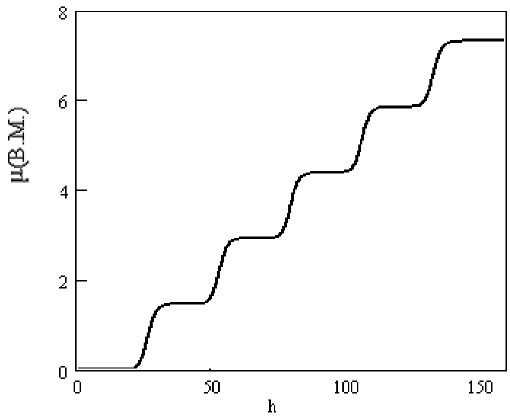

Fig. 1. Magnetic moment as a function of magnetic field from Ref.12.

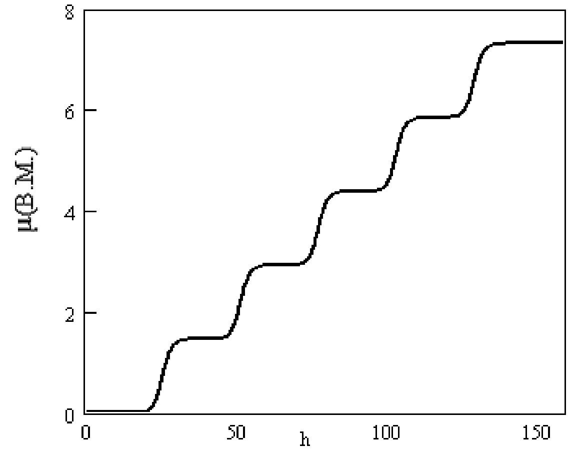

Fig. 2. Magnetic moment as a function of magnetic field from Ref.35.

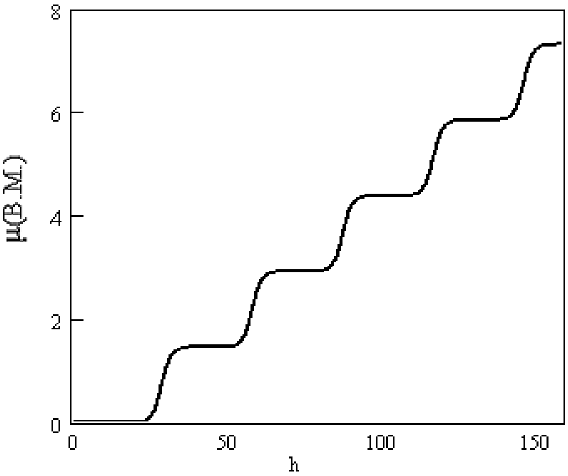

Fig. 3. Magnetic moment as a function of magnetic field from Refs.45and 46.

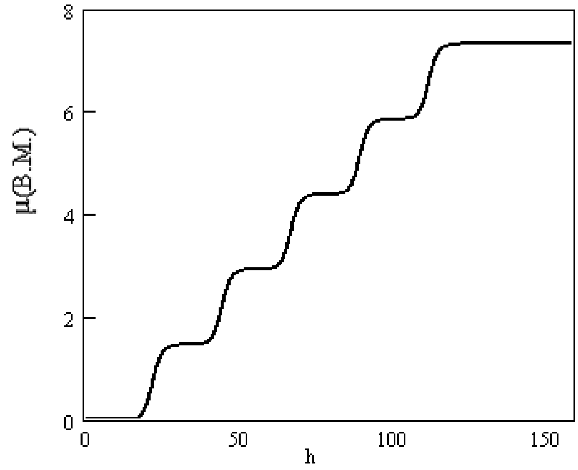

Fig. 4. Magnetic moment as a function of magnetic field from Ref. 47.

4. Conclusions

In this study we mainly concentrated on the magnetic moment of the Fe(II) ions in a magnetic field below a certain temperature. The temperature dependence of the susceptibility and the magnetization for the title complexes have already been reported by Elmalı et al.[12]. In our work it was clearly shown the magnetization shows a ladder like behavior below a certain temperature as is expected. It was also shown that the saturation magnetization can be more easily reached when the antiferromagnetic coupling is small.

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