acta physica slovaca vol. 51 No. 5, 281 – 287 PAGE PROOFS October 2001

BINUCLEAR IRON Fe(II) 3-SEMICARBAZONE-2,3 DIOXOINDOLE COMPLEXES AS POTENTIAL ORGANIC FERROMAGNETS

L. Valko[a,c], F. Hurta[b], M. Valko[c], J. Sláma[d], A. Košturiak[e]
[a] *Department of Physics, Trenčín University, Študentská 2, SK-911 50 Trenčín, Slovakia*
[b] *Department of Cybernetics, Trenčín University, Študentská 2, SK-911 50 Trenčín, Slovakia*
[c] *Department of Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovakia*
[d] *Department of Theoretical and Applied Electrical Engineering, Faculty of Information Technology and Electrical Engineering, Slovak Technical University, Ilkovičova 3, SK-812 19 Bratislava, Slovakia*
[e] *Department of Physical and Analytical Chemistry, P. J. Šafarik University, Moyzesova 11, SK-041 54 Košice, Slovakia*

Received 26 February 2001, in final form 19 August 2001, accepted 20 August 2001

The temperature dependence (220 - 470 K) of the magnetic susceptibility is reported for the organometallic molecular ferromagnet-chelates of the dinucleating Fe(II) 3-semicarbazone-2,3 dioxoindole ligand. An average antiferromagnetic exchange is present in the dinuclear Fe(II) chelates and is characterised by the coupling constant $J = -44.1 \times 10^{-4}$ eV and $g = 2.08$, where the spin-coupling Hamiltonian is taken as $H = -2J\boldsymbol{S}_1\boldsymbol{S}_2$ for Fe(II) centres; the susceptibility studies agree and fit with this result. This study verifies the existence of 3-semicarbazone-2,3 dioxoindole-bridged di-iron(II) centres. The temperature dependence of magnetic moment is illustrated.

PACS: 36.40.Cg, 75.50.-y, 75.50.Ee

1 Introduction

There is a growing interest in the study of dinuclear transition metal complexes derived from dinucleating ligands, where several electronic spins are coupled with dominant isotropic exchange integrals [1,2]. Among such polynuclear magnetic molecular materials are the magnetic polymeric materials which exhibit interesting magnetic behavior [3]. Amongst these are included a large variety of a new class of compounds which are either ferro or antiferromagnetic materials known as the organometallic polymeric materials, consisting of metal ions and organic ligands [4]. The most common magnetic polymers of this type consist of metal ions bridged by organic ligands forming polymeric structures through a network of hydrogen bonds. As regards the diversity of observed magnetic properties, this is by far the richest type of magnetic polymers. 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. In a strict sense they are not polymeric materials since repetitive units, e.g., monomers, are not interconnected by covalent bonds [5]. A large variety of magnetic phenomena, including ferromagnetism and metamagnetic behavior, have been observed in these materials [3]. The magnetic behavior of several compounds in this class of organometallic polymers beautifully illustrate some of the properties of amorphous magnetism [6]. Since such compounds present a certain degree of structural disorders and, in general, tend to be non-crystalline, it should be expected that they exhibit specific peculiarities in their magnetism and applicability. Therefore the properties that we can foresee for these materials have to be looked for in the context of the magnetism of amorphous solids. In this paper we present the experimental temperature dependence of the magnetic susceptibility of an organometallic magnetic polymer of antiferromagnetic ordering namely Fe(II) 3-semicarbazone-2,3 dioxoindole. The results presented are part of a more extensive program carried out in the cooperating laboratories dealing with the organometallic magnets.

2 Experimental

The preparation of ferromagnetic ordering in Cu-chelates of 3-thiosemicarbazone-2,3 dioxoindole and other magnetic data on the compounds studied have been given previously in [7]. The Fe-chelates were prepared in similar manner, e.g., the divalent iron salt has been complexed with the ligand $L \equiv$ 3-semicarbazone-2,3 dioxoindole to give an organometallic Fe(II) magnetic polymer with a general composition of Fe_2 $L_2(OH)_2$ where -OH is a coordinated group. All chemicals used were of analytical grade. The titled chelates were prepared by dissolving the appropriate amount of the ingredients in a water- ethanol solution. The solution was then heated to 80° C for about two hours and then slowly cooled. The precipitated complexes were filtered off and washed. The Fe(II) chelates obtained were purified by repeated recrystallization. The procedure for the preparation of the chelates has been discussed elsewhere [8]. It seems reasonable to assume that, in the coordinative reaction conditions, a certain amount of $Fe(OH)_2$ is also formed. If this is the case then oxidation with residual oxygen contained in the solvent produces α-FeO(OH) (goethite) which during the process of drying the complexes yields, $2FeO(OH) \rightarrow \alpha\text{-}Fe_2O_3 + H_2O$, small particles of iron oxides which, indeed, can contribute, as a ferric impurity, to the magnetic properties of material. The single crystal X-ray structure of these interesting chelates was not until now realized, since we were not successful in the preparation of a monocrystal of the titled polymeric material. In the framework of physical measurements the Mössbauer, infrared, and electronic spectra were obtained using standard instrumentation. The variable-temperature dependence of the effective magnetic susceptibility was measured by a full automatic device with a kappa bridge KLY - 2, between approximately 280 and 450 K. The measurements were performed on powdered amorphous organo-metallic samples of the titled Fe(II) chelates with a relatively small magnetic impurity. The apparatus and technique used to collect the data have been described elsewhere [9].

3 Calculation of the magnetic susceptibility

The essential differentiating characteristics between the structure of an amorphous solid and that of a crystalline one is the lack of translational periodicity. Hence, no long range structural order can be established in an amorphous solid [3]. In a supposedly amorphous magnetic polymer, bond and chemical disorder will tend to create a distribution of the magnitude moments and exchange interactions. Strictly speaking no magnetic order, either ferro- or antiferromagnetic, can be expected under these conditions. However, as long as the exchange interaction remains positive (parallel alignment), some spontaneous magnetization should be expected. The magnetic moments will tend to orient randomly within a solid angle. An aim is to find useful correlations between structure and magnetic coupling and in doing so to understand the factors which determine the extent of coupling between the iron ions as has been done for other similar magnetic polymers [10]. In organic solids, with a small or null magnetocrystalline anisotropy there is the possibility of different spin states arising from the interaction between the unpaired electrons on the individual metal ions in a polynuclear compound. What we require is a quantitative description of these interactions. A common characteristic is the strong dependency of the intensity of dipolar interactions with the distance and, in the case of superexchange interactions, with the bond angle. Usually in systems such as $Fe_2L_2(OH)_2$, because of their low symmetry of their local environment, the individual magnetic Fe(II) ions of the iron group are in singlet orbital electronic ground states. There is no first order contribution to the spin-orbit coupling and to a good approximation the g- factors of the various ions are isotropic and often close to the free electron value [11]. In its simplest form the exchange interaction is taken to be isotropic and to involve the coupling between the total spin angular moments on nearest neighbor paramagnet monomers. The direct Fe(II)$\cdots$Fe(II) exchange interaction may be written by the known spin Heisenberg-Dirac-van Vleck exchange model Hamiltonian [12]

$$H = \sum_{j>i,\ i=1}^{n} H_{ij} = -2 \sum_{j>i,\ i=1}^{n} J_{ij} S_i S_j, \tag{1}$$

where J_{ij} is an exchange integral between centres i and j , J_{ij} is negative for an antiferromagnetic interaction and positive for a ferromagnetic interaction and; S_i and S_j are the spin angular momentum operators appropriate to i and j, respectively. The molar magnetic susceptibility χ_m for a dinuclear complex for which the exchange integral $J_{12} = J$ between neighboring pairs of interacting paramagnetic ions with spin quantum numbers $S_1 = S_2 = S$, was given by Earnshaw et al [13] as

$$\chi_m = \left(\frac{N_A g^2 \mu_0 \mu_B^2}{k_B T}\right) \frac{\left\{\sum_{S_t} S_t(S_t+1)(2S_t+1)\Omega(S_t) e^{-E_{S_t}/k_B T}\right\}}{\left\{\sum_{S_t} (2S_t+1)\Omega(S_t) e^{-E_{S_t}/k_B T}\right\}}, \tag{2}$$

where μ_0 is the vacuum permeability, N_A is Avogadro's constant and S_t is the total electronic spin quantum number for a given coupled energy level of the dinuclear complex. If we consider the situation of entirely equivalent dinuclear interacting centres, van Vleck has derived the following expression for the energy of each of the spin states specified by $S_t = 2S, 2S-1, \ldots, 0$

$$E(S_t) = -J[S_t(S_t+1) - 2S(S+1)] \tag{3}$$

and at the same time considering $S_1 = S_2 = S$. It is possible that a given value of S_t may occur a number of times because of the different ways of combining the spins on the various centres, i.e. its degeneracy of a given S_t energy level is calculated from the expression

$$\Omega(S_t) = \omega(S_t) - \omega(S_t + 1), \tag{4}$$

where $\omega(St)$ is the coefficient of S_t in the expansion

$$\left(x^S + x^{S-1} + \cdots + x^{-S+1} + x^{-S}\right)^n, \tag{5}$$

where $x = -J/k_B T$ and n is the number of interacting paramagnetic ions.

In an external homogeneous magnetic field each of the energy levels specified by $E(S_t)$ will be split into $2S_t + 1$ components which are separated by $g\mu_B H$, where H is the applied field stress. Since we are dealing with antiferromagnetic systems the smallest values of S_t have the lowest energy. It is normally permissible to use van Vleck's susceptibility equation since only the levels which are likely to be thermally populated will satisfy the assumption that $E_i^{(1)} H \ll k_B T$ and $E_i^{(1)} H^2 \ll k_B T$, where $E_i^{(1)}$ and $E_i^{(2)}$ are the first- and second-order Zeeman coefficients respectively (it should be noted that these do not have dimensions of energy). However, some caution in applying van Vleck's equation to systems containing a large number of weakly interacting centres may be needed, such situation is important in the organometallic magnetic polymers studied herein since levels with large values of S_t, for which $E_i^{(1)} H$ may not be less than $k_B T$, may be thermally populated at the temperatures used to measure the magnetic susceptibilities.

It is well known that antiferromagnetism in the magnetic polymer $\mathrm{Fe(II)_2L_2(OH)_2}$ involves the direct interaction between electronic spins on neighboring metal Fe(II)$\cdots$Fe(II) atoms, however, the most obvious question which arises is "What is the mechanism of this interaction?" It is generally accepted that the mechanism of the exchange interaction involves the mutual pairing of electronic spins via some form of orbital overlap, analogous to the formation of a chemical bond. The following two mechanisms are usually involved to account for antiferromagnetic exchange: (a) direct Fe(II)$\cdots$Fe(II) interaction, and (b) indirect exchange interaction or superexchange interaction. The chemist is mainly interested in the discrete (intramolecular) antiferromagnetic interactions for the excellent reason that this is by far the commonest type of interaction in chemical compounds and that the concept is easier to understand than intermolecular interactions. However, the intermolecular interactions are very important and in some cases are dominant for an amorphous polymer magnetism. This type of interaction involves the interaction between unpaired electron spins with opposite spins on the two interacting ions -$\mathrm{OH^-}$ via an intermediate diamagnetic anion -$\mathrm{OH^-}$, e.g., Fe(III)-$\mathrm{OH^-}\cdots{}^-$H-O-Fe(III). To account for the indirect exchange interaction in the present work we have accepted the Griffiths et al. [14] idea, that a small admixture of an excited state in chelates could cause exchange interaction between the unpaired electron spin on each Fe(III) ion. This contribution to the superexchange interaction arises by transfering an electron from Fe(II) to vacant -OH molecular orbital. The chemistry of binuclear oxygen-bridged iron complexes has experienced a resurgence of interest with the discovery of bridged units containing Fe(III,III), Fe(III,II), and Fe(II,II). Such oxidation states have been investigated in the context of the increasing interest in oxygen-bridged binuclear Fe-units in biology, and models thereof, and in the phenomenon of ferromagnetism. The dipolar coupling approach of van Vleck with a perturbing Hamiltonian $-2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ and $S_1 = S_2 = 2$ was used to analyze the experimental susceptibility data. Using the Earnshaw et al Eq. (2) [13], for the

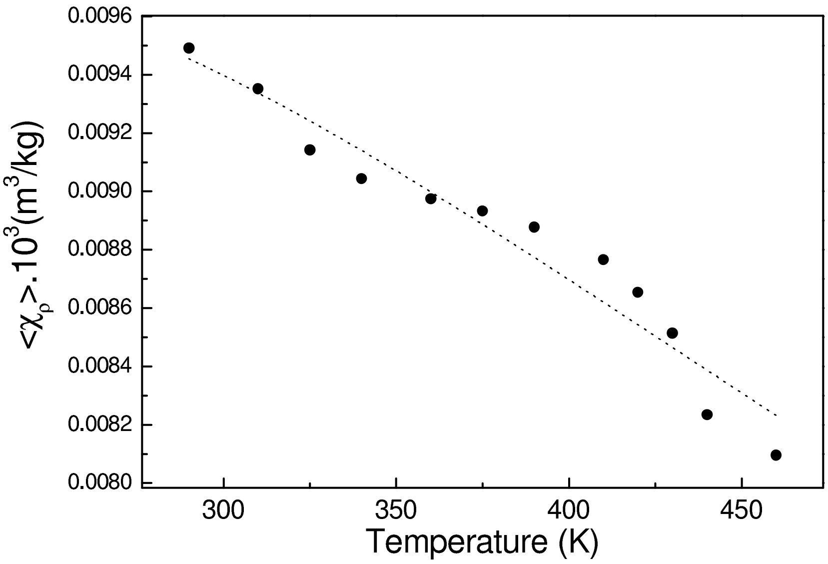

Fig. 1. Temperature dependence of the average mass magnetic $\langle\chi_\rho\rangle$ susceptibility for the amorphous magnetic polymer with binuclear monomer $Fe_2L_2(OH)_4$. The experimental points are shown as circles; the best fit is shown as the dotted line resulting from a least - squares fit to the theoretical equation for an isotropic exchange interaction.

mass magnetic susceptibility χ_ρ for the binuclear Fe(II) iron organometallic magnetic polymer we have obtained expression

$$\chi_\rho = \left(\frac{Ng^2\mu_0\mu_B^2}{k_BT}\right)\frac{60+28e^{-8x}+10e^{-14x}+2e^{-18x}}{9+7e^{-8x}+5e^{-14x}+3e^{-18x}+e^{-20x}} \tag{6}$$

where N is the number of Fe particles per unit mass (1kg).

Detailed magnetic, analytical and Mössbauer studies have been made on a number of binuclear Fe(II) complexes in an effort to determine the spin state for the Fe(III) ions. The over-all data are most consistent with evidence for the presence of iron (III) in the samples. The existence of a weak ferromagnetic impurity (α - Fe_2O_3) and above all the binuclear Fe(III) structures is assumed as a consequence of the superexchange interaction having the same diamagnetic susceptibility, molecular weight as the dinuclear complex, and to have a magnetic susceptibility that follows the Curie (Néel) law. To take these magnetic components into consideration, we express an average mass magnetic susceptibility $\langle\chi_\rho\rangle$ expression as

$$\langle\chi_\rho\rangle = \chi_\rho(1-p)+\frac{35Ng^2\mu_B^2}{12k_BT}p, \tag{7}$$

where χ_ρ is given by eq. (6), the parameter p gauges the presence of iron (III) and amount of possible magnetically dilute ferric impurity. Other symbols have their usual meaning. A nonlinear fitting routine on the parameters g, p, and J was used to fit the corrected experimental

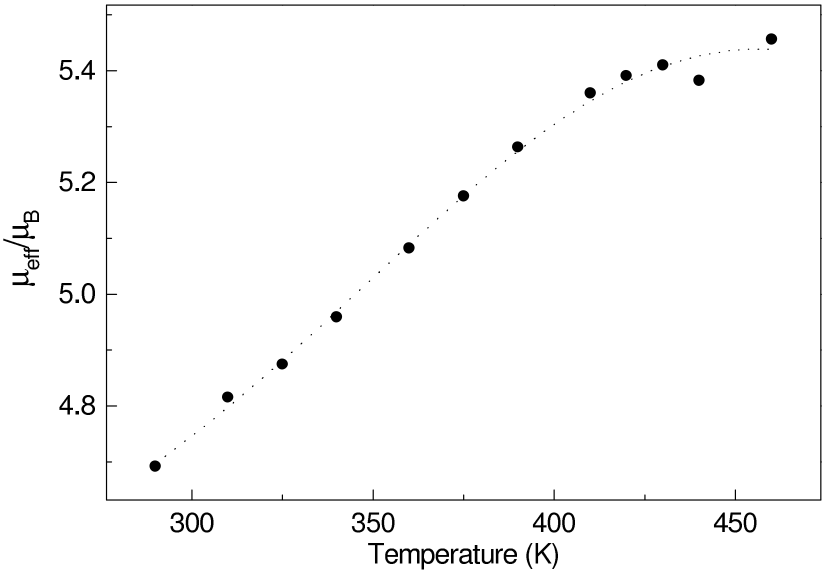

Fig. 1. Temperature dependence of the effective magnetic moment μ_{eff}/μ_B for $Fe_2L_2(OH)_4$ complex. The experimental points are shown as circles, the best fit is shown as the dotted line.

data to eq. (7). The temperature-independent paramagnetism was neglected. The best fit to the experimental data yielded $J = (-44.1 \pm 1.7) \times 10^{-4}$ eV, $g = 2.08 \pm 0.35$ and $p = 0.02$. These parameters fit the data quite well as is illustrated in Fig. 1. The data presented for the magnetic susceptibility of the dinucleaer Fe(II) complex have not been corrected for the diamagnetic susceptibility. We can conclude that the interpretation of the magnetic susceptibilities of dinuclear Fe(II) transition metal chelates studied involves the herein interaction of electrons with opposite spins on the two interacting intermediate diamagnetic -OH^- anions and this superexchange mechanism seems dominant. The effective magnetic moment is calculated from the mass magnetic susceptibility χ_ρ using the relation

$$\mu_{\mathrm{eff}} = \sqrt{\frac{3k_B T\langle\chi_\rho\rangle}{N\mu_0}} \tag{8}$$

The temperature dependence of the effective magnetic moment per iron ion, μ_{eff}/Fe is illustrated in Fig. 2 and varies from 4.70μ_B at ~280 K to 5.43μ_B at ~450 K. Magnetic susceptibility measurements above ~460 K were not carried out since organometallic polymer decomposes at this temperature.

4 Discussion

$Fe_2L_2(OH)_2$ may be considered as among one of the first genuine organo-metallic polymeric ferromagnets. This organometallic polymer exhibits an antiferromagnetic exchange interaction, with the best fit to the van Vleck equation yielding $J = -44.1 \times 10^{-4}$ eV and with $g = 2.08$. The data presented supports the idea that the magnetic polymer is best represented as two directly interacting Fe(II)$\cdots$Fe(II) centres and with superexchange interaction which with is probably realized through a network of hydrogen -OH$\cdots$OH bridges which comprehensively show relatively weak spin coupling with the exchange values, usually ranging in the case of the antiferromagnetic materials roughly within the interval -24.8×10^{-4} to -49.6×10^{-4} eV [15]. Probably the displacement of the Fe (II) metal ion from the L ligand plan, together with the addition of a more ferromagnetic exchange pathways due to additional unpaired electrons, leads to a reduction in the net antiferromagnetic interaction. A crystal structure, of course, required to ascertain the exact displacement of the iron Fe(II) ions in this organometallic polymer.

Acknowledgement: This investigation has been partially supported by the VEGA grant (to J. S., M. V. and A. K.).

References

[1] U. Casellato, P. A. Vigato, M. Vidali: *Coord. Chem. Rev.* **23** (1977) 31

[2] S. E. Groh: *Isr. J. Chem.* **15** (1977) 277

[3] F. Palacio, J. Ramos, C. Castro: *Mol. Cryst. Liq. Cryst.* **232** (1993) 173

[4] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi: *in Magnetic Molecular Materials*, (Eds. D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio). Kluwer, Acad. Publ. 1990, p. 198, p. 233

[5] C. P. Landee: *in Organic and Inorganic Low-dimensional Crystalline Materials*, (Eds. P. Delhaes, M. Drillon). Plenum Pub. Corp., New York 1987, B 168, p. 75

[6] F. J. Lazaro, M. C. Morón, J. Reyes, J. Garin, F. Palacio: *Sol. State Comm.* **80** (1991) 969

[7] M. Zentková, J. Kováč, A. Zentko, A. Košturiak: *J. Magn. Magn. Mater.* **102** (1991) L1

[8] A. Košturiak, L. Valko, J. Polavka: *Slovak Patent 279 309* (1999)

[9] A. Grusková, J. Sláma, M. Miglierini, L. Valko, R. Vicen, R. Dosoudil: *J. E. Engineering* **46** (1995) 46

[10] T. Kaneyoshi: *Amorphous Magnetism*, CRC Press, Boca Raton 1984

[11] E. Belorizky, P. H. Frie: *J. Chim. Phys.* **90** (1993) 1077

[12] J. H. van Vleck: *Theory of Electric and Magnetic Susceptibilities*, Oxford University, Press, London and NewYork 1932, Chap. 12

[13] A. Earnshaw, B. N. Figgis, J. Lewis: *J. Chem. Soc. A* (1966) 1656

[14] J. H. Griffiths, J. Owen, J. G. Park, M. F. Partridge: *Proc. R. Soc. A* **250** (1959) 84

[15] W. M. Reiff, G. J. Long, W. A. Baker, Jr.: *J. Am. Chem. Soc.* **90** (1968) 6347