JOURNAL OF OPTOELECTRONİCS AND ADVANCED MATERİALS Vol. 10, No. 3, March 2008, p. 589 - 591

Sizeable amount of antiferromagnetic exchange interactions in newly reported dimeric cobalt (II) complex of the antiprine Schiff base of 3-formylsalicylic acid

F. M. AVCU[a], Ö. AYTEKIN[b], M. KARAKAPLAN[c], A. BAYRI[b]
[a]*Inonu University, Department of Informatics, Tr-44069 Malatya, Turkey*
[b]*Adıyaman University, Arts and Science Faculty, Department of Physics, Tr-02020 Malatya, Turkey*
[c]*Inonu University, Arts and Science Faculty, Department of Chemistry, Tr-44069 Malatya, Turkey*

This study reports the magnetic properties of newly reported cobalt(II) complex of the antiprine Schiff base of 3-formylsalicylic acid. Assuming the isotropic Heisenberg model is valid it is suggested that there is a sizeable amount of antiferromagnetic exchange interactions between metal centers in dimeric units. It is also suggested that the system become demagnetized below a certain temperature.

(Received September 11, 2007; accepted March 12, 2008)

Keywords: Magnetization, Magnetic susceptibility, Cobalt(II) complex, Antiferromagnetic exchange

1. Introduction

The magnetization of transition metal complexes is important to coordination chemistry since magnetic behavior is generally effected by coordination geometry and the electronic configuration of paramagnetic ions. Almost always it is not difficult to understand the magnetism for most of the first transition metals simply because the orbital contribution to the magnetic moment is negligible and only spin angular momentum should be considered. On the other hand, for octahedral high spin $3d^7$ complexes orbital angular momentum contribution cannot be neglected. For such a case the effect of spin-orbit coupling should be taken into account for magnetism calculations [1-9]. Thus, the magnetic calculations for mononuclear octahedral cobalt(II) complexes is quite complex, while for other first-transition elements are relatively simple. Many approximate method have been introduced for the calculation of the magnetic moment of a high-spin octahedral cobalt(II) complexes in an axially distorted octahedral field considering the axial field splitting Δ and the spin-orbit coupling λ[7,10,11], which are successful for mononuclear cases. But for polynuclear case many problems arise. In 1971 Lines reported a theory for the analysis of magnetic exchange interaction between two high-spin cobalt(II) ions of pure O_h symmetry which was successful for the analysis of magnetic data in highly symmetrical dinuclear cobalt(II) complexes [12]. Recently synthesis and characterization of cobalt(II), nickel(II), copper(II), palladium(II) and dioxouranium (VI) complexes of the antipyrine Schiff base of 3-formylsalicylic acid was reported[13]. From their structural investigation by spectral, thermal and magnetic data it was argued that while dinuclear complexes of cobalt(II), nickel(II), copper(II) and dioxouranium(VI) have been synthesized, the palladium(II) complex was mononuclear square planar. From their magnetic susceptibility measurements it is quite clear that there is a considerable antiferromagnetic interactions between those magnetic centers in all paramagnetic dinuclear complexes, which was also mentioned by the authors[13]. The main interest in this study is to understand the behavior and the amount of exchange interactions between those magnetic centers in dimeric units. Recently I tried to explain the antiferromagnetic interactions in dinuclear nickel(II) units [14]. As it was mentioned above the cobalt(II) is much more complicated than the copper(II) and nickel(II) ions since it has some orbital contribution to the magnetic moment. In this study we mainly concentrate on the magnetic behavior of newly reported cobalt(II) dimmer[13] and tried to find out the amount of antiferromagnetic exchange coupling(J) and the ordered phase transition temperature. Since the orbital contribution to the magnetic moment will bring some extra complications when analyzing the magnetic data, it is assumed that the orbital contribution would be completely quenched such that the isotropic Heisenberg model can be used. It is important to note that this assumption is nearly valid only when the ground term is ^4A or ^4E. Although this assumption is quite far away from the reality, it may give some true reflection of real mechanism. It should be pointed out here that in order to obtain a deeper understanding of true mechanism some of possible discrepancies should be included to all calculations.

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 [1,3,4,15,16]:

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

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

$$H = -\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot \vec{D}_i \cdot \vec{S}_i + \mu_B \sum_i \vec{S}_i \cdot \vec{g}_i \cdot \vec{B} \quad (1)$$

where *i* and *j* runs over all spin centers, $\vec{D}_i$ and $\vec{g}_i$ denote Cartesian tensors [1,3,15].

3. Average magnetic moment and magnetic susceptibility of dimeric Co^{2+} ions

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

$$H = -J\vec{S}_1 \cdot \vec{S}_2 \quad (2)$$

where *H* consists of the isotropic exchange term. The isotropic interaction phenomenon is purely electrostatic in nature [1,3,15]. 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

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \quad (3)$$

hence

$$\vec{S}^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2 \quad (4)$$

The Hamiltonian may be rewritten as

$$H = -\frac{J}{2}\left(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2\right) \quad (5)$$

the eigenvalues of which are

$$E(S,S_1,S_2) = -\frac{J}{2}[S(S+1) - S_1(S_1+1) - S_2(S_2+1)] \quad (6)$$

which, after a change of origin, can be rewritten

$$E(S) = -\frac{J}{2}S(S+1) \quad (7)$$

where S will take the values of 2S, 2S-1, …, 0 . It is important to stress that the HDVV Hamiltonian is easy to handle. Once the energy spectrum of isotropic Heisenberg Hamiltonian is found, then the magnetic susceptibility can be calculated by using the well known formula of Van Vleck as [1,3,15,17-19]

$$\chi(T) = \frac{N\beta^2 g^2}{3kT}\frac{\sum_S S(S+1)(2S+1)\exp-\left(\frac{E(S,S_1,S_2)}{kT}\right)}{\sum_S (2S+1)\exp-\left(\frac{E(S,S_1,S_2)}{kT}\right)} \quad (8)$$

and magnetic moment as [17-19]

$$m(T,B) = N\beta g\frac{\sum_S \sinh\left(\frac{2S+1}{2}y\right)SB_S(Sy)\exp\left(-\frac{E(S,S_1,S_2)}{kT}\right)}{\sum_S \sinh\left(\frac{2S+1}{2}y\right)\exp\left(-\frac{E(S,S_1,S_2)}{kT}\right)} \quad (9)$$

where $y = \frac{g\beta B}{kT}$ and $B_S(S,y)$ is the Brillouin function. Since cobalt (II) ion has three unpaired electron , there are four possible values of S, i.e. 3, 2, 1 and 0, with the energies -6J, -3J, -J, and 0, respectively. In this particular case the equations are almost trivial. Since the reported room temperature magnetic moment of abovementioned cobalt(II) complex is 2.64 B.M.[13] our issue is to find what particular value of J would yield this observed magnetic moment at room temperature. It is clear that this value is obtained when $\chi(T)\cdot T = 0.87146318188$. Since the reported magnetic data is observed at room temperature it seems the needed amount of J should be -199 cm^{-1}. For this particular value of J the variation of magnetic moment for temperature is shown in Fig.1.

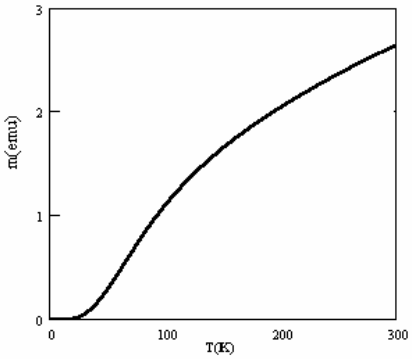

Fig. 1. Temperature variation of magnetic moment of cobalt(II) dimmer for J=-199 cm^{-1}.

According to our approach it seems below 25 K the system becomes demagnetized. i.e. below this temperature the orientations of magnetic moments in the dimmer would be antiparallel. Whether this temperature and the value for J is close enough to the correct value or not

should be tested with experimental data. So we hope that some temperature dependent magnetic data will be carried out for this purpose, which would not be too difficult to get this data from a vibrating sample magnetometer.

5. Conclusion

In this study we tried to find out the amount of exchange interactions in newly reported cobalt(II) complex. It should be noted that the approach, adopted in this study, has many approximations. So the calculated value should not be considered as the correct value for this complex but certainly it has some true reflection of the real interaction mechanism. Hopefully, an experimental test for the transition temperature would be a good test for testing the accuracy of the approach used in this study.

References

[1] O. Kahn. Molecular Magnetism. VCH, New York 1993.
[2] R. D. Willet, D. Gatteschi, O. Kahn, Magneto-Structural Correlation in Exchange Coupled Systems, Nato ASI series, Reidel, Dordrecht, 1983.
[3] H. J. Zeiger, G. W. Pratt. Magnetic Interactions in Solids. Clarendon Pres. Oxford, 1973.
[4] F. E. Mabbs, D. J. Machin, Magnetism and Transition Metal Complexes, Chapman and Hall, London, 1973.
[5] B. N. Figgis, J. Lewis. Modern Coordination Chemistry. Interscience, 1960.
[6] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962
[7] A. Bayri, A. R. Bahadır, F.M. Avcu, Ö. Aytekin, Transition Metal Chemistry. **30,** 987 (2005).
[8] I. B. Bersuker, Electronic Structure and Properties of Transition Metal Componds, John Wiley & Sons, Inc., 1996.
[9] B. N. Figgis. Introduction to Ligand Fields, Interscience, 1966.
[10] M. E. Lines, Phys. Rev. **131**, 546 (1963).
[11] B. N. Figgis, Trans. Faraday Soc. **57**, 198 (1961).
[12] M. E. Lines, J. Chem. Phys. **55**, 2977 (1971).
[13] J. K. Nag, S. Pal, C. Sinha, Transition Met. Chem. **30**, 523 (2005).
[14] A. Bayri, J. Inorganic and Orgonametallic polymers and materials **16**(1), 97 (2005).
[15] F. Isik, S. Ekmekçi, A. Bayri, J. Optoelectron. Adv. Mater. **8**(5), 1856 (2006).
[16] A. Bayri, M. Sulu, Journal of Inorganic and Organometallic Polymers and Materials **16**(2), 185 (2006).
[17] A. Bayri, Modern Physics Letters B **20**(28), 1803 (2006).
[18] A. Bayri, N. Raman, Optoelectron. Adv. Mater. – Rapid Comm. 1(12), 712 (2007).
[19] J. Rojo, M. Lehn, G. Baum, D. Fenske, O. Waldmann, P. Muller. Eur. J. Inorg. Chem. 517 (1999).

*Corresponding author: fatih@inonu.edu.tr