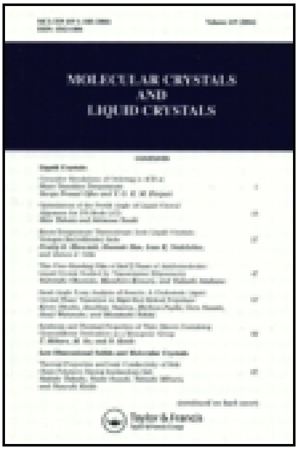

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Roman Boča, Karsten Falk & Wolfgang Haase (1999): Non-Linear Magnetic Behavior of a Tetranuclear Copper(II) Cluster, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 33-42

To link to this article: http://dx.doi.org/10.1080/10587259908028849

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 33-42
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Printed in Malaysia

Non-Linear Magnetic Behavior of a Tetranuclear Copper(II) Cluster

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A tetranuclear copper(II) cluster, namely $[Cu_4OCl_6(mor)_4]$, mor – morpholine, has been investigated by the magnetization measurements at the temperature as low as 1.74 and 2.73 K, respectively. A numerical derivative yielded the differential magnetic susceptibility. The low-temperature magnetization data were fitted to a two dimensional function $M = f(B,T)$ and the following set of magnetic parameters has been obtained: $g = 2.351$, $J_a/k = -6.33$ K and $J_b/k = -0.76$ K. These parameters determine the spacing of energy levels in a tetranuclear cluster of the C_{3v} symmetry.

Keywords: magnetization; copper(II) cluster; exchange interactions

INTRODUCTION

It is frequently assumed that molecular complexes and clusters in the magnetic fields of a moderate strength (up to 1.5 T) behave exclusively like linear magnetics. In such a case the treatment outlined by van Vleck is fully justified[1]. The zero-field energies modified by the magnetic field enter the terms of the partition function and when the Zeeman factor is low and temperature high, i.e.,

$$y = \frac{\mu_B g B M_S}{kT} << 1 \tag{1}$$

then an expansion of the exponentials is possible. Under these circumstances, for instance, the Brillouin function can be substituted for a linear dependence and consequently one gets the Curie law for mononuclear substances[2]. Alternatively, a determination of the first- and second-order van Vleck coefficients makes the van Vleck equation useful in deriving analytic formulae for the magnetic susceptibility of a variety of substances[3].

For higher magnetic fields and low temperature, on the contrary, the relationship (1) is not fulfilled, $y \approx 1$, and thus non-linear magnetic behavior can appear. Expansion of the exponential terms is no longer possible and one has to deal with the true magnetic partition function.

Another important aspect lies in the fact that the mean magnetic susceptibility, introduced through a simple ratio of the magnetization and the magnetic field strength ($B = \mu_0 H$) as

$$\bar{\chi} = \mu_0 \frac{M}{B} \tag{2}$$

looses its battle; a true thermodynamic quantity is represented by the differential magnetic susceptibility

$$\tilde{\chi} = \mu_0 \left(\frac{\partial M}{\partial B} \right) \tag{3}$$

The declination of the mean magnetic susceptibility from the differential one may be substantial at low temperature and high field[4]. The differential magnetic susceptibility is directly recorded in alternating magnetic fields, using an AC susceptometer.

THEORY

Let the isotropic exchange Hamiltonian with the following sign convention is considered

$$\hat{H}^{\rm iso} = -\sum_{i<j} J_{ij}(\vec{S}_i \cdot \vec{S}_j)[\hbar^{-2}] \qquad (4)$$

For an exchange coupling within a tetranuclear cluster of spins $S_1 = S_2 = S_3 = S_4 = 1/2$ the sixteen energy levels, at the tetrahedral arrangement of centers are represented by two singlets, three triplets and one quintet which in the magnetic field are split as follows

$$\varepsilon_{S=0,M_S=0}(B) = 0 \qquad (5a)$$

$$\varepsilon_{S=1,M_S=0,\pm 1}(B) = -J + \mu_{\rm B} gBM_S \qquad (5b)$$

$$\varepsilon_{S=2,M_S=0,\pm 1,\pm 2}(B) = -3J + \mu_{\rm B} gBM_S \qquad (5c)$$

or

$$\varepsilon_{S,M_S}(B) = \varepsilon_S(B=0) + \mu_{\rm B} gBM_S = -n_S J + \mu_{\rm B} gBM_S \qquad (6)$$

The molar magnetization is introduced as a thermal average of the microscopic magnetic moments, hence

$$M_{\rm mol} = N_{\rm A} \frac{1}{Z} \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i / kT) \qquad (7)$$

with the partition function

$$Z = \sum_{S=S_{\rm min}}^{S_{\rm max}} Z(S) = \sum_{S=S_{\rm min}}^{S_{\rm max}} \sum_{M_S=-S}^{+S} \exp[(n_S J - \mu_{\rm B} gBM_S)/kT] \qquad (8)$$

The molar differential magnetic susceptibility is obtained as

$$\tilde{\chi}_{\rm mol} = \mu_0 \left(\frac{\partial M_{\rm mol}}{\partial B} \right) \qquad (9)$$

and since the second-order derivatives are zero for the isotropic exchange model, a simple form is obtained

$$M_{\mathrm{mol}} = N_{\mathrm{A}} \frac{1}{Z} T_1 \tag{10}$$

and

$$\tilde{\chi}_{\mathrm{mol}} = \frac{N_{\mathrm{A}}\mu_0}{kT} \frac{1}{Z^2}(T_2 Z - T_1^2) \tag{11}$$

The terms of the magnetization and the susceptibility are

$$\begin{aligned} T_1 &= \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B}\right) \exp(-\varepsilon_i / kT) = \\ &= \mu_{\mathrm{B}} g \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_{\mathrm{B}} g B M_S) / kT] \end{aligned} \tag{12}$$

$$\begin{aligned} T_2 &= \sum_i \left(\frac{\partial \varepsilon_i}{\partial B}\right)^2 \exp(-\varepsilon_i / kT) = \\ &= (\mu_{\mathrm{B}} g)^2 \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_{\mathrm{B}} g B M_S) / kT] \end{aligned} \tag{13}$$

and they are evaluated in Table I.

For a more complex situation, when the trigonal distortion of the cluster polyhedron to the C_{3v} symmetry is considered, two exchange coupling constants, J_a and J_b, have to be introduced. Analogously for the tetragonal distortion leading to the S_4 symmetry one should differentiate between the interdimer (J_a) and the intradimer (J_b) coupling constants. Both more complex models of either C_{3v} or S_4 symmetry recover the model of the T_d symmetry in the limit of $J_a = J_b = J$.

A modeling of the magnetization has been done assuming either a slight ferromagnetic ($J/k = +2$ K) or an antiferromagnetic ($J/k = -2$ K) interaction. Two-dimensional mesh diagrams are presented in Fig. 1. Notice, for the antiferromagnetic case the magnetization shows a step increase which predetermines that the differential magnetic susceptibility is an oscillating function of the magnetic induction (Fig. 2.).

TABLE I Terms of the magnetic susceptibility for a tetranuclear cluster with $S_i = 1/2$ [a]

Z	$T_1/(\mu_B g)$	$T_2/(\mu_B g)^2$
a) regular tetrahedron: $x = J/kT$		
$2 \cdot 1 +$	$0 +$	$0 +$
$+3 \cdot \exp(x+y)$	$+3 \cdot 1 \cdot \exp(x+y)$	$+3 \cdot 1^2 \cdot \exp(x+y)$
$+3 \cdot \exp(x)$	$+0$	$+0$
$+3 \cdot \exp(x-y)$	$-3 \cdot 1 \cdot \exp(x-y)$	$+3 \cdot 1^2 \cdot \exp(x-y)$
$+1 \cdot \exp(3x+2y)$	$+1 \cdot 2 \cdot \exp(3x+2y)$	$+1 \cdot 2^2 \cdot \exp(3x+2y)$
$+1 \cdot \exp(3x+y)$	$+1 \cdot 1 \cdot \exp(3x+y)$	$+1 \cdot 1^2 \cdot \exp(3x+y)$
$+1 \cdot \exp(3x)$	$+0$	$+0$
$+1 \cdot \exp(3x-y)$	$-1 \cdot 1 \cdot \exp(3x-y)$	$+1 \cdot 1^2 \cdot \exp(3x-y)$
$+1 \cdot \exp(3x-2y)$	$-1 \cdot 2 \cdot \exp(3x-2y)$	$+1 \cdot 2^2 \cdot \exp(3x-2y)$
b) trigonal distortion to C_{3v} symmetry: $x_1 = -3(J_a + J_b)/2kT$, $x_2 = -2J_b/kT$, $x_3 = -(3J_a + J_b)/2kT$		
$1 \cdot \exp(x_1) +$	$0 +$	$0 +$
$+1 \cdot \exp(x_2+y)$	$+1 \cdot 1 \cdot \exp(x_2+y)$	$+1 \cdot 1^2 \cdot \exp(x_2+y)$
$+1 \cdot \exp(x_2)$	$+0$	$+0$
$+1 \cdot \exp(x_2-y)$	$-1 \cdot \exp(x_2-y)$	$+1 \cdot 1^2 \exp(x_2-y)$
$+2 \cdot \exp(x_3+y)$	$+2 \cdot 1 \cdot \exp(x_3+y)$	$+2 \cdot 1^2 \cdot \exp(x_3+y)$
$+2 \cdot \exp(x_3)$	$+0$	$+0$
$+2 \cdot \exp(x_3-y)$	$-2 \cdot 1 \cdot \exp(x_3-y)$	$+2 \cdot 1^2 \cdot \exp(x_3-y)$
$+1 \cdot \exp(2y)$	$+1 \cdot 2 \cdot \exp(2y)$	$+1 \cdot 2^2 \cdot \exp(2y)$
$+1 \cdot \exp(y)$	$+1 \cdot 1 \cdot \exp(y)$	$+1 \cdot 1^2 \cdot \exp(y)$
$+1 \cdot 1$	$+0$	$+0$
$+1 \cdot \exp(-y)$	$-1 \cdot 1 \cdot \exp(-y)$	$+1 \cdot 1^2 \cdot \exp(-y)$
$+1 \cdot \exp(-2y)$	$-1 \cdot 2 \cdot \exp(-2y)$	$+1 \cdot 2^2 \cdot \exp(-2y)$

[a] Substitution $y = B\mu_B g/kT$.

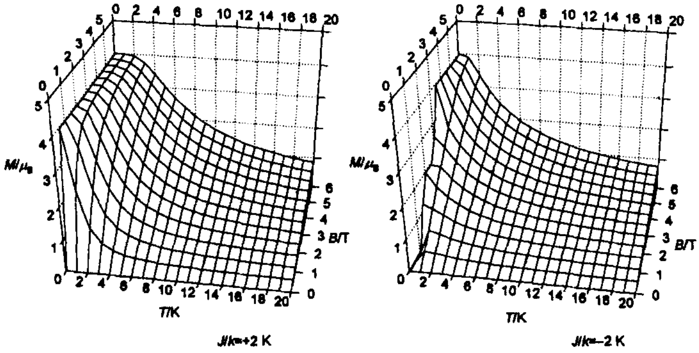

FIGURE 1 Modeling of the magnetization per cluster for a tetrahedral $S_1 = S_2 = S_3 = S_4 = 1/2$ system, $M = f(B,T)$.

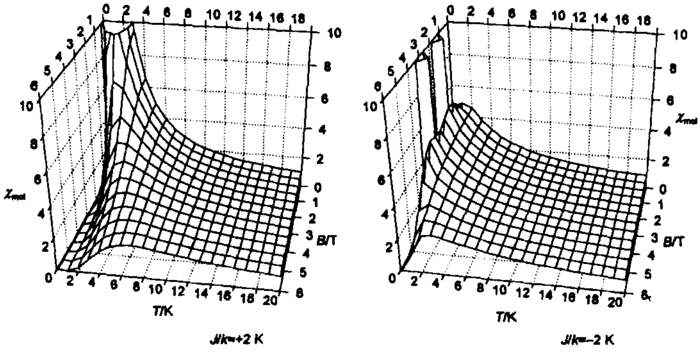

FIGURE 2 Modeling of the molar differential magnetic susceptibility (in units of 10^{-6} m^3 mol^{-1}) for a tetrahedral $S_1 = S_2 = S_3 = S_4 = 1/2$ system, $\widetilde{\chi}_{\rm mol} = f(B,T)$.

RESULTS AND DISCUSSION

The structure of the cluster under the investigation – [$Cu_4OCl_6(mor)_4$] has already been established by the X-ray structural analysis[5] and it is displayed in Fig. 3. The bond lengths show that the central cluster is slightly distorted in a trigonal manner: the Cu–Cu bond lengths are 3.091, 3.093, 3.090, 3.107, 3.132 and 3.149 Å.

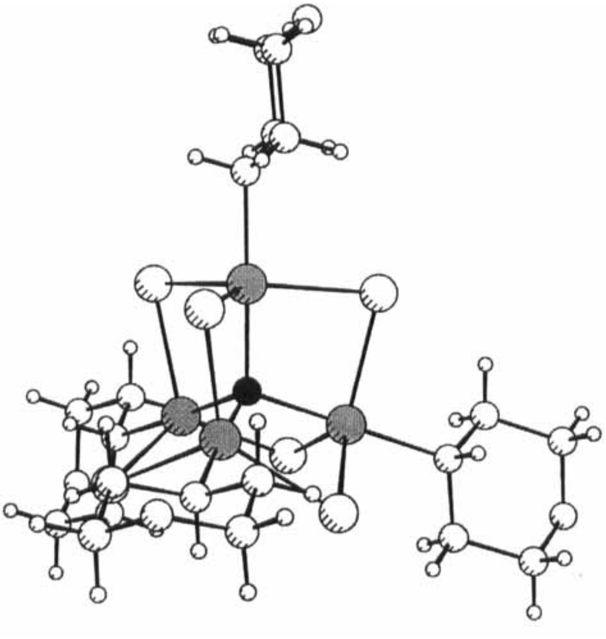

FIGURE 3 Molecular structure of [$Cu_4OCl_6(mor)_4$].

The experimental magnetization data for [$Cu_4OCl_6(mor)_4$], as recorded with an AC susceptometer/magnetometer (LakeShore, model 7225), are displayed in

Fig. 4. It can be seen that the cluster evidently behaves like a non-linear magnetics. The magnetization data at the constant temperature, $M = f(B)$, have been numerically differentiated and thus the differential magnetic susceptibility has been reconstructed. This is plotted in Fig. 4 (right) along with the experimental reading of the field dependence of the AC (differential) susceptibility.

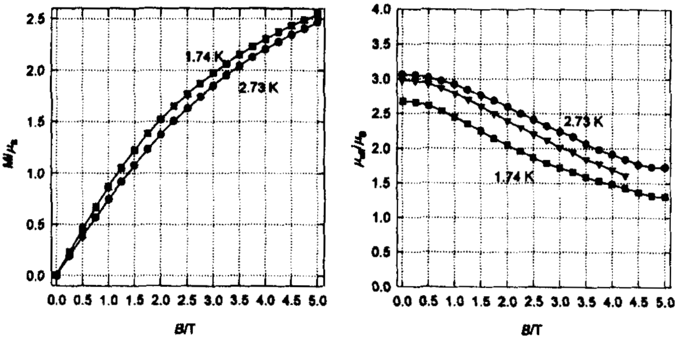

FIGURE 4 Experimental data (left) on magnetization per particle *vs.* magnetic induction: circles – $T = 2.73$ K, squares – $T = 1.74$ K; right - reconstructed differential magnetic susceptibility function transformed to the effective magnetic moment; triangles - experimental data at $T = 2.73$ K.

The experimental magnetization data have been used to fit the theoretical magnetization formula (10) where three magnetic parameters occur: $M = f(B;[T],g,J_a,J_b)$. In a more advanced fitting procedure the two-dimensional function has been considered: $M = f(B,T;g,J_a,J_b)$. The magnetic parameters as they result from the fitting procedure are collected in Table II.

TABLE II Calculated magnetic parameters from the magnetization data.[a]

C_{3v} symmetry	$T = 2.73$ K	$T = 1.74$ K	$T = 1.74$ & 2.73 K
g	2.485	2.280	2.351
$(J_a / k)/\mathrm{K}$	−8.34	−5.96	−6.33
$(J_b / k)/\mathrm{K}$	−0.16	−0.77	−0.76
R/%	0.17	0.78	4.41
Number of points	21	21	42

[a] Range: $B = 0 - 5$ T.

It can be seen that in the cluster under the investigation the antiferromagnetic interaction within a base triad dominates ($J_a / k \approx -6$ K). This is completed by a weaker antiferromagnetic coupling between the base triangle and the apical vertex of the trigonal pyramid ($J_b / k \approx -1$ K). The assumption of a regular tetrahedron does not lead to acceptable results (the g-factor is then too low: $g = 1.5$).

The problem of the exchange coupling in $\{Cu_4O\}$-type clusters resonated in 70-ties (say [6-8]) where in explaining the maximum on the temperature dependence of the effective magnetic moment the antisymmetric exchange has been included [9]. Even more complex models have been introduced later [10] and critically discussed in connections with the ESR data [11]. However, any of these models brings an additional splitting of energy levels of the tetrahedral pattern (see eqns. (5)) which, evidently, is an incorrect model. The splitting of the zero-field energy levels is obtained not only through the inclusion of more "exotic" exchange coupling terms but also simply by reducing the symmetry of the complex and considering the isotropic exchange alone [12]. This is exactly what was applied in our data analysis and fitting.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft and Volkswaagen-Stifung for support.

References

[1] J.H. van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, 1932).
[2] R.L. Carlin, *Magnetochemistry* (Springer, Berlin, 1986).
[3] O. Kahn, *Molecular Magnetism* (VCH Publishers, New York, 1993).
[4] R. Boča, *Coord. Chem. Rev.*(1998), in press.
[5] P. Weinberger, R. Schamschule, K. Mereiter, L. Dlháň, R. Boča, and W. Linert, *J. Mol. Struct.,* **446,** 115 (1998).
[6] J.A. Barnes, G.W. Inman and W.E. Hatfield, *Inorg. Chem.,* **10,** 1725 (1971).
[7] R.F. Drake, V.H. Crawford and W.E. Hatfield, *J. Chem. Phys.,* **60,** 4525 (1974).
[8] H. Wang, H. tom Dieck, C.J. O'Connor and E. Sinn, *J. Chem. Soc., Dalton Trans.,* 786 (1980).
[9] M.E. Lines, A.P. Ginsberg, R.L. Martin and R.C. Sherwood, *J. Chem. Phys.,* **57,** 1 (1972).
[10] A.M. Leushin and N.N. Sutugin, *Solid State Phys. (Rus.),* **19,** 2087 (1977).
[11] A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems*(Springer, Berlin, 1990).
[12] D.H. Jones, J.R. Sams and R.C. Thompson, *J. Chem. Phys.,* **79,** 3877 (1983).