

Very High-Field Magnetization and Intermolecular Interactions: Application to $\{[tmen(2-MeIm)Cu]_2(C_2O_4)\}(PF_6)_2$ (tmen = N,N,N',N' -Tetramethylethylenediamine, 2-MeIm = 2-Methylimidazole)

Pierre Bergerat,[†] Olivier Kahn,^{*,†} Patrick Legoll,[‡] Marc Drillon,[‡] and Maurice Guilloit[§]

Laboratoire de Chimie Inorganique, URA No. 420, Université de Paris Sud, 91405 Orsay, France, Groupe des Matériaux Inorganiques, Institut de Physique et Chimie des Matériaux de Strasbourg, UM No. 46, 1 rue Blaise Pascal, 67008 Strasbourg, France, and Service National des Champs Intenses, UPR No. 5021, 38042 Grenoble, France

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Magnetic susceptibility measurements are nowadays routinely used to determine the sign and magnitude of the interaction between spin carriers in coupled molecular species. Most often, the experiments are performed in the solid state, and the intermolecular effects cannot be completely ignored. These intermolecular effects are rather easily detected when the molecular ground state is magnetic. This happens when the species is ferromagnetically coupled or when there is no compensation of the spin momenta within the molecular unit, for instance in antiferromagnetically coupled heteropairs.¹ In such cases, the low-temperature limit of the product $\chi_M T$ (molar magnetic susceptibility times temperature) differs from what a purely molecular model predicts. On the other hand, when the ground state is diamagnetic, whatever the nature of the intermolecular interactions may be, $\chi_M T$ tends to zero as T approaches absolute zero. Moreover, the low-temperature susceptibility data may be perturbed by the presence of a very small amount of uncoupled impurity. In other words, the magnetic susceptibility data for a coupled system with a diamagnetic ground state are only weakly sensitive to intermolecular interactions. Sometimes, a mean-field correction is applied to account for intermolecular effects.² For a system with a $S = 0$ spin ground state, such a correction at best may indicate the sign and the order of magnitude of the intermolecular effects. Very often, it is just a way to account for the inaccuracy of the experimental data.

Our goal in writing this note dealing with very high-field magnetization measurements on a copper(II) binuclear compound is twofold: (i) first, we will show that these measurements reveal the inadequacy of a purely molecular model; (ii) then, we will indicate how it is possible to determine accurately both intra- and intermolecular interaction parameters.

The compound we have investigated is $\{[tmen(2-MeIm)Cu]_2(C_2O_4)\}(PF_6)_2$; tmen stands for N,N,N',N' -tetramethylethylenediamine, and 2-MeIm, for 2-methylimidazole.^{3,4} The structure consists of centrosymmetric oxalato-bridged copper(II) binuclear dications, as shown in Figure 1, and PF_6^- anions. The environment of the copper atom is intermediate between a square pyramid with only one oxygen atom of the oxalato bridge, O2, in the basal plane, and a trigonal bipyramid with N1--Cu--O2 as the pseudotrigonal axis. The temperature dependence of the magnetic susceptibility (see Figure 2) has been interpreted with the binuclear model. The maximum of χ_M at 10.8 K indicates a $S = 0$ ground state. Least-squares fitting of the data led to a singlet–triplet

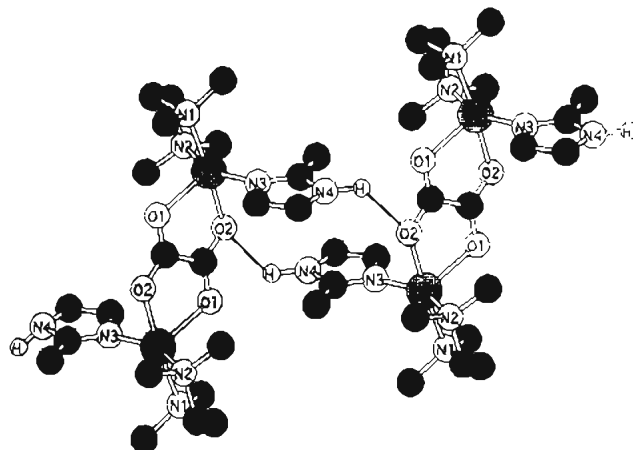


Figure 1. Perspective view showing two nearest neighbor binuclear cations $\{[tmen(2-MeIm)Cu]_2(C_2O_4)\}^{2+}$ along with the intermolecular interaction pathways. Reprinted with permission from ref 3. Copyright 1984 American Chemical Society.

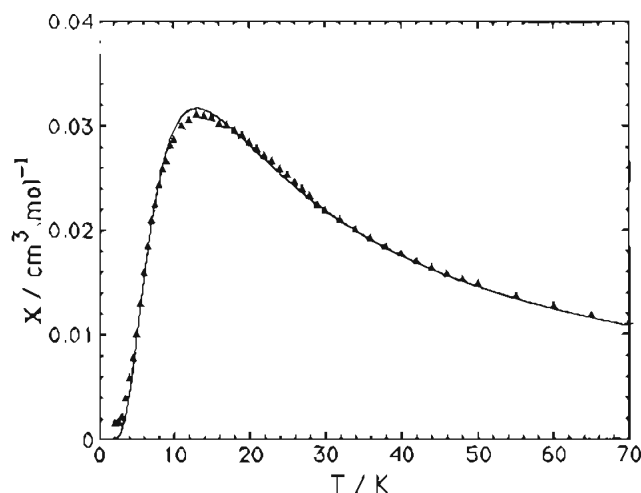


Figure 2. χ_M versus T plot for $\{[tmen(2-MeIm)Cu]_2(C_2O_4)\}(PF_6)_2$.

energy gap of $J = -13.8 \text{ cm}^{-1}$ (the interaction Hamiltonian is defined as $H = -JS_A \cdot S_B$, where S_A and S_B are the local spin operators), the Zeeman factor being found as $g = 2.08$. The agreement factor defined as $\sum[(\chi_M)^{obs} - (\chi_M)^{calc}]^2 / [(\chi_M)^{obs}]^2$ was found as 5.22×10^{-4} , which corresponds to a very satisfying theory–experiment agreement, so that no attempt to introduce a mean-field correction was made. Therefore, before we measured the high-field magnetization, we thought we were faced with quite a simple case of isolated antiferromagnetically coupled binuclear units.

The dependence of the magnetization M versus the magnetic field H for such a system is given by⁵

$$M = 2Ng\beta \frac{\sinh(g\beta H/kT)}{\exp(-J/kT) + 1 + 2 \cosh(g\beta H/kT)} \quad (1)$$

where the symbols have their usual meaning. For a critical value of the field defined as $H_c = -J/g\beta$, there is a crossover between the singlet state and the Zeeman component $M_S = -1$ arising from the triplet state. It follows that at very low temperature ($|kT/J| \ll 1$) the $M = f(H)$ plot should exhibit an abrupt transition at H_c , with a change of sign of the second derivative $\partial^2 M / \partial H^2$. In the present case, H_c is expected to be around 140 kOe.

The field dependence of M has been measured at two temperatures, 3 and 4.2 K, up to 200 kOe. The experimental

[†] Université de Paris Sud.

[‡] Institut de Physique et Chimie des Matériaux de Strasbourg.

[§] Service National des Champs Intenses.

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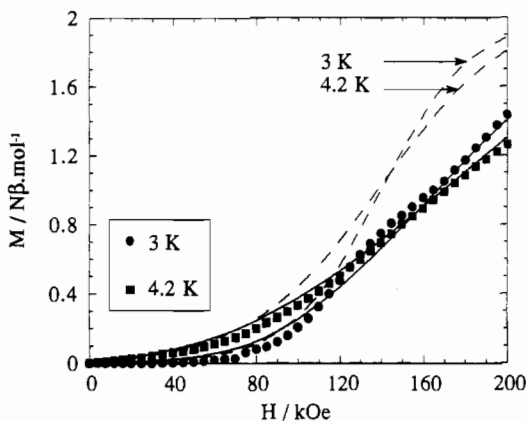


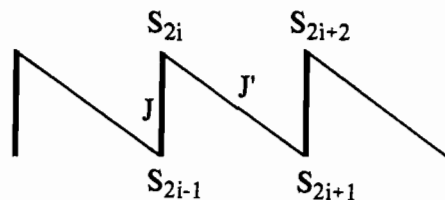
Figure 3. Magnetization versus magnetic field plots for $\{tmen-(2-Melm)Cu\}_2(C_2O_4)(PF_6)_2$: ●, at 3 K; ■, at 4.2 K; dotted lines, theoretical curves for a purely molecular model; full lines, theoretical curves for a model taking into account intermolecular effects.

data are represented in Figure 3 together with the curves deduced from eq 1. One immediately sees that the experimental data do not follow at all the theoretical behavior expected for a purely molecular model. In particular, the transition around 140 kOe with a change of sign for $\partial^2 M/\partial H^2$ is much less pronounced than expected. The first idea coming to mind is that the singlet and triplet molecular states are strongly coupled, so that the crossover at H_c is avoided. This idea, however, can be ruled out. Indeed, the only mechanism able to couple significantly singlet and triplet states in a copper(II) pair is the antisymmetric interaction described phenomenologically by a perturbation of the form $d \cdot S_A \wedge S_B$. For a centrosymmetric pair, however, the d vector vanishes.⁶⁻⁹ Therefore, we must admit that the molecular model is not valid, even if the magnetic susceptibility data can be interpreted in the frame of such a model. The high-field magnetization data point out the role of intermolecular interactions.

A careful look at the crystal structure reveals that the nitrogen atom N4 of the 2-Melm ligand is hydrogen-bonded to both oxygen atoms, O1 and O2, of the oxalato bridge belonging to a neighboring dication. The intermolecular separations are N4- -O1 = 3.39 Å, H(N4)- -O1 = 2.44 Å and N4- -O2 = 3.15 Å, H(N4)- -O2 = 2.40 Å.

What is crucial to understanding the magnitude of the intermolecular interaction is the orientation and the delocalization of the copper(II) magnetic orbital.³ If the copper(II) environment was strictly square pyramidal with the N1, N2, N3, and O2 atoms in the basal plane, the spin delocalization toward O2 would be large and that toward O1 would be almost zero. Actually, the copper(II) environment has some trigonal bipyramidal character, which may provide a nonnegligible spin density on O1. An extended Hückel calculation, however, suggests that the spin density on O1 remains very weak. This calculation leads to the following spin populations on the atoms surrounding the copper(II) ion: $p_{N1} = 0.074$, $p_{N2} = 0.056$, $p_{N3} = 0.050$, $p_{O2} = 0.054$, $p_{O1} = 0.003$. Of course, this calculation gives a rough estimate of the spin delocalization but does not provide any information on the spin polarization.¹⁰ In summary, the intermolecular interactions are essentially propagated through the Cu- -N3- -N4- -H- -O2- -Cu pathway, as emphasized in Figure 1.

In order to account for the field dependence of the magnetization, we considered a chain of binuclear units



with both intramolecular J and intermolecular J' interaction parameters.¹¹ The magnetization M is defined as

$$M = N g \beta \frac{\sum_n M_{S,n} \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \quad (2)$$

where E_n is the energy of the n th level in the presence of the magnetic field and $M_{S,n}$ is the quantum number associated with the spin operator $S_{z,n}$. The E_n 's are deduced from the spin Hamiltonian

$$H = -J \sum_i S_{2i} \cdot S_{2i-1} - J' \sum_i S_{2i} \cdot S_{2i+1} + g \beta \sum_i S_i \cdot H \quad (3)$$

The energy matrix associated with H was solved for a number N of interacting binuclear units ranging from 1 to 6, using the same numerical procedure as the one developed by Bonner and Fisher for linear chains.¹² Thus, the spin space symmetry was taken into account (the commutators $[H, S_x]$ and $[H, S_y]$ vanish, and rings of $2N$ spins were assumed to avoid border effects). It follows that the eigenfunctions of H transform as the irreducible representations of the point group D_N instead of D_2 . The results show that for $N = 6$ a quasi-continuum of the state density is reached in the region of interest. These were used for the least-squares fitting with the same set of parameters of both the temperature dependence of the susceptibility and the field dependence of the magnetization at 3 and 4.2 K. These parameters were found as $J = -14.0 \text{ cm}^{-1}$ and $J' = -5.6 \text{ cm}^{-1}$ with $g = 2.08$. The ratio J'/J is therefore equal to 0.4. The intermolecular interaction parameter, J' , is far from being negligible although it could not be deduced from the magnetic susceptibility data. The compound has a significant one-dimensional character, which clearly could not be anticipated from the mere examination of the crystal structure. This situation arises from the fact that two symmetry-related magnetic orbitals within a binuclear unit do not point to each other. It can be also noticed that J' corresponds to two intermolecular interaction pathways (see Figure 1). To the best of our knowledge, only high-field magnetization measurements could allow us to determine quantitatively the J and J' parameters. Specific heat measurements should exhibit a Shottky anomaly around 7 K, but it is not always easy to separate the magnetic and lattice contributions and further to deduce the interaction parameters when competing interactions take place. EPR could also be used to detect the magnetic dimensionality⁶ but could not provide a quantitative J' value. In the present case, the X-band powder EPR spectrum is that of a rhombic signal with $g_1 = 2.04$, $g_2 = 2.07$, $g_3 = 2.27$ at 98 K. The g_1 and g_2 values do not vary versus temperature; on the other hand, there is a very weak shift of g_3 which is equal to 2.25 at 10 K. As expected, the intensity of the signal shows a maximum at 10 K and then decreases rapidly as the temperature is lowered further.

To conclude, we wish to emphasize again the richness and the character often unique to the information that very high-field

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magnetization measurements can afford in the field of molecular magnetism.¹³⁻¹⁶

Experimental Section

$\{[\text{tmn}(2\text{-MeIm})\text{Cu}]_2(\text{C}_2\text{O}_4)\}(\text{PF}_6)_2$ was synthesized as already described.³ The magnetic susceptibility measurements were performed with

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a SQUID magnetometer down to 1.7 K, at a magnetic field of 10^3 Oe. The high-field magnetization measurements were performed at the Service National des Champs Intenses by means of a fluximetric method. The sample was extracted in a constant magnetic field between compensated pick-up coils connected in series opposition. The integrated signal of the induced voltage was proportional to the magnetization. The continuous magnetic field up to 200 kOe was produced by a water-cooled Bitter magnet. The calibration and the sensitivity of the apparatus were previously described in detail.¹⁷

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