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Spin relaxation in a ferromagnetically coupled triangular Cu_3 complex

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ABSTRACT

The trinuclear complex $[Bu_4N]_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$ (pz = pyrazolato anion) (**1**) exhibits ferromagnetic interactions resulting in an $S = 3/2$ ground state which is characterized by a small zero field splitting tensor [17]. Herein, the $S = 3/2$ state is further characterized using High-Frequency and -Field Electron Paramagnetic Resonance spectroscopy. The spin relaxation properties of **1** are studied with alternating current susceptometry in the presence of external magnetic fields. In the 4.5–8.0 K temperature range, the system relaxes via an Orbach mechanism involving transitions between the $S = 3/2$ and the excited $S = 1/2$ spin manifolds.

1. Introduction

The spin relaxation of Polynuclear Transition Metal Clusters (PTMCs) is one of the most intensely studied issues in the field of Molecular Magnetism [1]. The fascinating properties of a class of metal clusters, known as single molecule magnets (SMMs) [2] stem from the specific mechanism that governs the spin reversal in such systems [1]. From a biological perspective, PTMCs are found at the active sites of such important systems as ferritin, numerous iron–sulfur proteins and the oxygen evolving complex of Photosystem II. Their magnetic relaxation, often monitored by magnetic resonance spectroscopic techniques, is a tool to unveil critical information related to their structure and function [3–5].

Alternating current (*ac*) susceptometry is an appropriate technique for the elucidation of the dynamics of magnetization in synthetic PTMCs [1]. With this technique the complex susceptibility, $\chi = \chi' - i\chi''$ of the compound is monitored as a response to an oscillating magnetic field. The complex susceptibility is given by the generalized Debye model [1,6]:

$$\chi = \chi_S + \frac{\chi_T - \chi_S}{1 + (i\omega\tau)^{1-\alpha}} \quad (1)$$

where χ_T and χ_S are the susceptibilities at zero and infinite frequency, respectively, ω is the excitation frequency, τ is the relaxation time and α is a parameter between 0 and 1 which relates to the distribution of relaxation times. For a narrow distribution of the relaxation times $\alpha \to 0$, whereas $\alpha \to 1$ for an infinitely broad distribution.

With this technique the relaxation properties of transition metal complexes have been studied since the late 1930s [7–10]. For these compounds, *ac* susceptometry is carried out in the presence of external magnetic fields, H_{DC}. In the class of PTMCs, *ac* susceptometry has been an indispensible tool to characterize the behavior of SMMs [1]. Usually, the observation of a nonzero χ'' (out-of-phase) below a certain (blocking) temperature in the absence of an external magnetic field is a good indication that a particular PTMC might be an SMM [1]. A number of SMMs appear to have relatively low blocking temperatures (<1.8 K) [11–16], and in zero applied magnetic fields only the tail of out-of-phase signals are observed down to 2.0 K. Such a behavior has been attributed to fast relaxation due to quantum tunneling effects. Application of moderate magnetic fields suppresses this mechanism and the maxima in the out-of-phase signals shift toward higher temperatures [11–16].

A few years ago, the preparation and magnetic studies of the trinuclear Cu(II) complex $[Bu_4N]_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$ (**1**) where pz = pyrazolato anion was reported [17] (Fig. 1). The complex consists of a planar $Cu_3(\mu\text{-}pz)_3Cl_3$ metallacycle, capped unsymmetrically by two μ_3-Cl-atoms on either side. It has D_{3h} molecular symmetry, but is distorted away from ideal geometry in crystalline form (crystallographic 2-fold symmetry, with the rotation axis running through Cu1 and bisecting a pyrazole ring). The Cu-centers are in a N_2Cl_3 trigonal bipyramidal coordination environment, with N-atoms occupying the axial and Cl-atoms the equatorial positions. Previous magnetic studies showed that the magnetic interactions between the Cu(II) ions are ferromagnetic resulting in an $S = 3/2$ ground state. X-band Electron Paramagnetic Resonance (EPR) studies at 77 K on powder samples of **1** indicated that this state is characterized by a zero field splitting tensor with a small value ($|D_{3/2}| \sim 0.08\ cm^{-1}$). Clearly, cluster **1** does not meet any of the established criteria for observation of noteworthy magnetic relaxation properties akin to SMMs: neither the spin of the ground state nor the zero field splitting tensor

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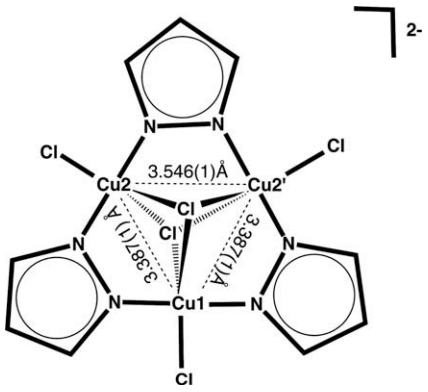

Fig. 1. Line drawing of the structure of the complex anion **1**.

have the values required to induce any appreciable barrier for spin reversal within this state.

Whereas the literature regarding application of *ac* susceptibility studies of SMMs is extensive, relatively few PTMCs that do not belong to this class have been studied with this method, so far. The necessity for elaborating on the magnetic properties of simple PTMCs clusters, such as **1**, has been outlined [18]. In the present work we study the magnetic relaxation properties of **1** by means of *ac* susceptibility measurements in order to explore its magnetic relaxation behavior. In the absence of an external magnetic field, no out-of-phase signals are observed. However, out-of-phase signals are induced in the presence of magnetic fields at liquid helium temperatures, allowing the study of the magnetic relaxation properties of this particular cluster. Important information related to the magnetic structure of the complex which could not be obtained by direct current (*dc*) magnetic susceptibility measurements, is revealed. The *ac* susceptibility studies are complemented with High-Frequency and -Field EPR (HFEPR) that verifies the previous results obtained at low frequency/field conditions and provides further information about the zero field splitting of the $S = 3/2$ ground state.

2. Experimental

2.1. Sample preparation

Powder samples of complex **1** were prepared from stoichiometric amounts of $CuCl_2{\cdot}2H_2O$, pyrazole, NaOH and $[Bu_4N]Cl$, as previously described ([17] and references therein).

2.2. EPR spectroscopy

HFEPR spectra were recorded using a home-built transmission-mode spectrometer at the Electron Magnetic Resonance (EMR) Facility of the National High Magnetic Field Laboratory (NHMFL, Tallahassee, FL, USA). The instrument differs from its detailed description in [19] only by the employment of a source manufactured by Virginia Diodes Inc. (Charlottesville, VA) operating at a base frequency of 12–14 GHz and multiplied by a cascade of multipliers. The simulations were performed with the program SPIN developed by Dr. A. Ozarowski, NHMFL, Tallahassee, FL.

2.3. Magnetic measurements

Alternating current (*ac*) susceptibility measurements were performed in the Institute of Materials Science, NCSR Demokritos, Greece, using a Quantum Design PPMS. Measurements were carried out in the 11–10 000 Hz and 0–60 kOe ranges with a parallel oscillating field of 5 Oe. Diamagnetic contributions were estimated from Pascal's constants.

3. Results and discussion

3.1. EPR studies

At 77 K the X-band EPR powder spectrum of **1** is characterized by an EPR spectrum consistent with an $S = 3/2$ state [17]. For an $S = 3/2$ system the pertinent spin Hamiltonian is [20]:

$$H_{3/2} = D_{3/2}\left(S_z^2 - \frac{5}{4}\right) + E_{3/2}\left(S_x^2 - S_y^2\right) + \beta\vec{H}_{DC}\tilde{g}_{3/2}\vec{S} + \sum_{i=1,2,3}\vec{I}_i\tilde{A}_i\vec{S} \quad (2)$$

where $D_{3/2}$ and $E_{3/2}$ stand for the zero field splitting parameters and β is the Bohr magneton. In the present work we extended the EPR studies to higher frequencies and lower temperatures with the intention of (a) separating the field-dependent Zeeman term in Eq. (2) from the field-independent fine and hyperfine terms, and (b) determining the sign of D. The last term in Eq. (2) represents the hyperfine interaction of the total spin with the three $^{63/65}$Cu nuclei. In the spectra shown below there are no resolved hyperfine features. For this reason this term was not included in the simulations. The effect of the hyperfine interaction was treated as an effective contribution to the line-width of the spectra.

A 224 GHz spectrum of **1** at 77 K is shown in Fig. 2. As expected, it shows a good resolution of parallel and perpendicular turning points for all three allowed $\Delta M_S = \pm 1$ transitions within the $S = 3/2$ state of the cluster. The parallel peaks unequivocally determine parameters $|D_{3/2}|$, and g_z, which are $0.088(2)\,cm^{-1}$, and 2.243(2), respectively. The values of $|E_{3/2}|$ and $g_{x,y}$ are intercorrelated and thus cannot be uniquely determined. In the simulations the same rhombicity factor $E/D = 0.1$ as determined previously at X-band [17] and the values of $g_{x,y} = 2.066$ and 2.076, respectively were used. Simulations at 77 K cannot determine the sign of $D_{3/2}$, therefore we performed HFEPR at 4.2 K and at a somewhat lower

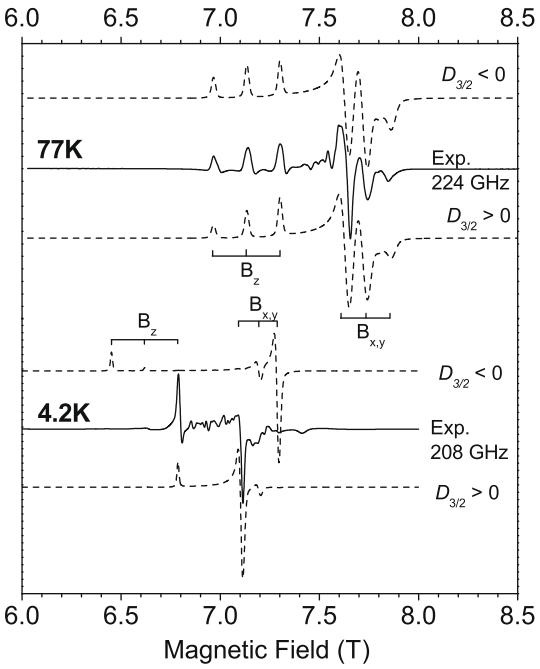

Fig. 2. EPR spectra of **1** at 77 K and 224 GHz (top solid trace) and 4.2 K and 208 GHz (bottom solid trace). The dashed lines are simulations assuming a perfect powder pattern for an $S = 3/2$ spin state and use the following spin Hamiltonian parameters: 77 K: $D_{3/2} = \pm 0.088\ cm^{-1}$, $E_{3/2} = \mp 0.009\ cm^{-1}$, $\tilde{g}_{3/2} = [2.066, 2.076, 2.243]$; 4.2 K: $D_{3/2} = \pm 0.088\ cm^{-1}$, $E_{3/2} = 0$, $\tilde{g}_{3/2} = [2.064, 2.064, 2.245]$.

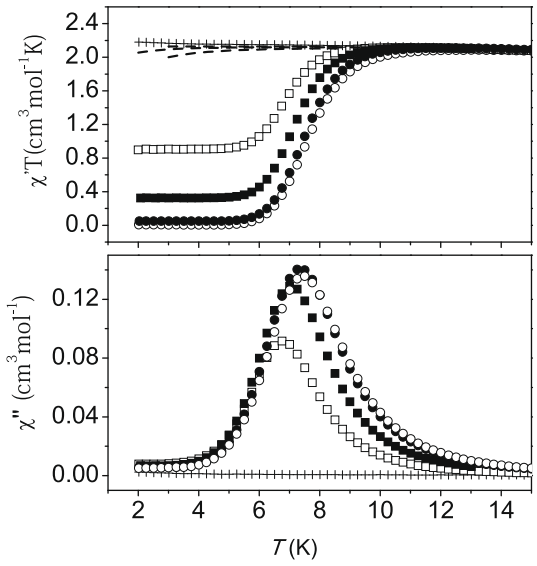

Fig. 3. $\chi'T$ vs T (upper panel) and χ'' vs T (lower panel) at 5638 Hz. Magnetic fields: 0 (+), 1 kOe (□), 2 kOe (■), 5 kOe (●) and 10 kOe (○). Dashed lines in the upper panel are simulations on the basis of Eq. (3) for H_{DC} = 1.0, 5.0 and 10 kOe.

frequency of 208 GHz (Fig. 2). Because the 4.2 K spectrum does not correspond to a perfect powder pattern, we simulated it with a simplified, axial set of spin Hamiltonian parameters. Despite this simplification, one can clearly see the effect of reversing the sign of $D_{3/2}$ on the intensities of both parallel and perpendicular turning points. Simulations show that the sign of $D_{3/2}$ is unambiguously positive. Therefore, in zero field the $S = 3/2$ state splits into two Kramers doublets with $M_S = \pm 1/2$ and $\pm 3/2$ and the former has the lowest energy. The absolute value of $|D_{3/2}|$ agrees well with the previously determined value of 0.075(5) cm^{-1}, and the g values remain in good agreement, too.[1]

In conclusion HFEPR studies at low temperatures in the solid state verify the $S = 3/2$ ground state of the system. Moreover, the sign and magnitude of the zero field splitting tensor are accurately determined. This information will be used to evaluate the relaxation properties presented below.

3.2. ac Susceptibility measurements

The temperature dependence of the magnetic susceptibility of **1** was reported earlier [17]. The EPR properties indicate that the $S = 3/2$ ground state is characterized by a zero field splitting tensor of the order of ~0.09 cm^{-1}. Due to this term the spin quartet splits into two Kramers doublets separated by $\Delta_{3/2} \sim 0.18$ cm^{-1} in the absence of an external magnetic field. No remarkable magnetic relaxation properties are anticipated within this state, in view of the relatively small spin and zero field splitting values.[2]

In Fig. 3, we show the temperature dependence of the product $\chi'T$ recorded at various external magnetic fields, H_{DC} and an *ac* frequency of 5638 Hz. The dashed lines represent simulations of the $\chi'T$ vs T data expected for the three interacting Cu(II) $S_i = 1/2$ ions within the (isotropic) exchange Hamiltonian:

$$H_{EXC} = \sum J_{ij}\vec{S}_i\vec{S}_j + \beta\vec{H}_{DC}\sum \tilde{g}_i\vec{S}_i \quad \text{with } i,j = 1,2,2' \tag{3}$$

For these simulations we used $\tilde{g}_i \equiv g = 2.13$ taken from EPR spectroscopy. Moreover, we assumed equal exchange coupling constants, $J_{ij} = J$ (see below). We mention that the value of the zero field splitting of the $S = 3/2$ ground state as determined by the EPR studies is too small ($|D_{3/2}| < 0.1$ cm^{-1}) to affect the $\chi'T$ vs T curves calculated by the isotropic exchange model of Eq. (3).

For $H_{DC} = 0$, the $\chi'T$ product increases smoothly as the temperature decreases and the data are well simulated within the above model with $J = -24$ cm^{-1}, in good agreement with the results from the earlier study [17]. In agreement with Casimir–Du Pre theory [7] no out-of-phase signals ($\chi'' = 0$) are induced for $H_{DC} = 0$. For $H_{DC} \neq 0$, the $\chi'T$ vs T curve follows the theoretically predicted one until T = 7–9 K. Below these temperatures a characteristic drop of $\chi'T$ is observed which indicates slow relaxation. Indeed, concurrently with the drop of χ', characteristic out-of-phase signals ($\chi'' \neq 0$) are induced (Fig. 3). Similar behavior is found for other frequency values.

The field induced χ'' exhibits characteristic dependence upon frequency and temperature. The data for selected frequencies for H_{DC} = 2.0 kOe are shown in Fig. 4. At 9111 Hz, the peak maximum, T_{max} is ~7.5 K. As the frequency decreases the peak maximum shifts to lower temperatures and at 10 Hz is below 2.0 K. From the maxima of these plots we may derive the relaxation time τ as a function of temperature. The temperature dependence of $\ln\tau$ for selected magnetic field values is shown in Fig. 5. A few ferromagnetic trinuclear clusters have been studied by *ac* susceptometry in the presence of external magnetic fields [23]. In these cases the out-of-phase signals were much weaker than those shown in Fig. 3 and they did not exhibit the characteristic temperature and frequency dependence shown in Fig. 4.

Two temperature regions can be recognized for all field values in Fig. 5. For $T > 4.5$ K, $\ln\tau$ depends linearly upon $1/T$. For $T < 4.5$ K, a characteristic curvature in the dependence of $\ln\tau$ on $1/T$ is observed. This change depends on the value of the external magnetic field H_{DC} and is more pronounced for low fields.

To study further the behavior of the relaxation of **1**, plots of $\chi''(\omega)$ vs $\chi'(\omega)$ for given conditions (T, H_{DC} – the so called Cole–Cole plots) [1,6] were constructed. Fig. 6 shows representative Cole–Cole plots, while Fig. 7 shows the dependence of parameter α on temperature derived from the analysis of Cole–Cole plots on

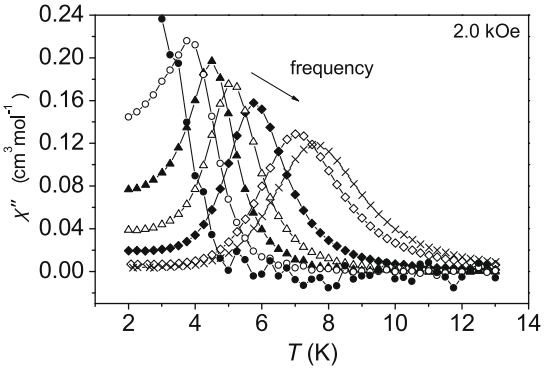

Fig. 4. Out-of-phase *ac* susceptibility vs T at H_{DC} = 2.0 kOe for **1** in a 5 Oe *ac* magnetic field oscillating at 18 Hz (●), 75 Hz (○), 196 Hz (▲), 511 Hz (△), 3362 Hz (♦), 5638 Hz (◇) and 9111 Hz (×). Solid lines are a guide to the eye.

[1] At 77 K the $S = 1/2$ states have a considerable degree of thermal occupation (the ratio of the $S = 3/2$ and 1/2 states populations is *ca.* 2 at this temperature). While we do not know the spin Hamiltonian parameters for the $S = 1/2$ states, the turning points of the corresponding spectra should appear in Fig. 2. Although there are some features in the 77 K trace in Fig. 2 that cannot be simulated using the $S = 3/2$ state parameters, they are probably due to imperfections in the random distribution of microcrystallites, as is the case at 4.2 K. The failure to observe the EPR spectra of the thermally accessible excited states in some Cu_3 clusters has been noted before [21,22] and remains an open question.

[2] In Ref. [17] the temperature dependence of the magnetic susceptibility was monitored by measuring χ' with an *ac* susceptometer in the presence of a magnetic field H_{DC} of 10 Oe. As we show here relaxation effects are observed at significantly larger magnetic fields.

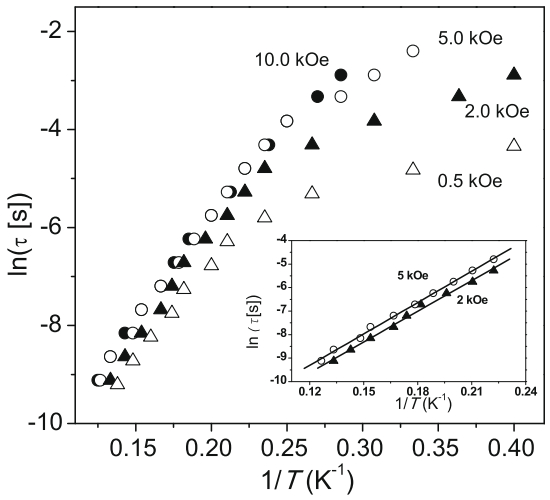

Fig. 5. Dependence of ln τ on $1/T$ for selected magnetic fields. The inset focuses on temperatures above 4.5 K for H_{DC} = 2.0 and 5.0 kOe. Solid lines are fits as described in the text.

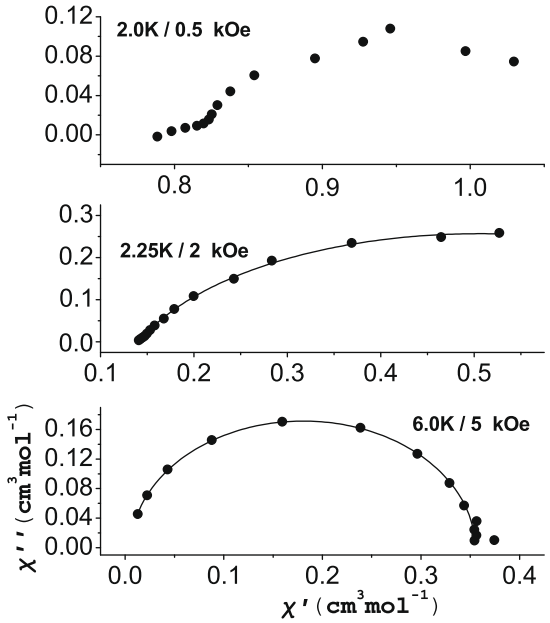

Fig. 6. Cole–Cole plots under various conditions. Solid lines are theoretical simulations on the basis of the generalized Debye model [24].

the basis of the generalized Debye model [24] for 2.0, 5.0 and 10 kOe. As in the case of the dependence of the relaxation times on temperatures (Fig. 5), the Cole–Cole plots exhibit different behavior above and below 4.5 K.[3] The following discussion focuses on the $T > 4.5$ K region.

For $T > 4.5$ K, the (χ', χ'') points fall in a semicircle with the parameter $\alpha \sim 0$ for all magnetic field values (Fig. 7). Therefore, a single relaxation process with a narrow distribution of relaxation times is implied. The linear dependence of ln τ on $1/T$ suggests that this thermally activated process may be modeled on the basis of the Orbach mechanism [20]:

[3] Measurements have been carried out up to 60 kOe. Under high field values the magnetization of the system reaches the conditions for saturation at relatively high temperatures. This results in weak χ' and χ'' signals the analysis of which is not reliable.

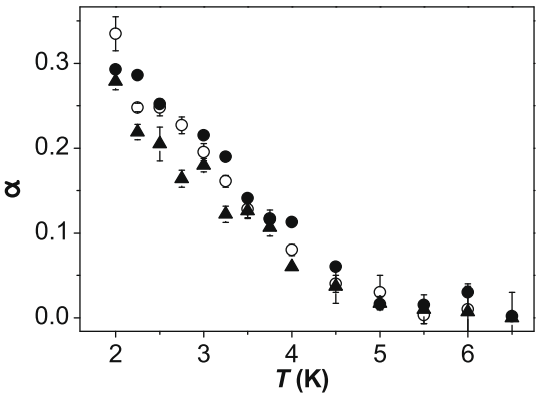

Fig. 7. Dependence of parameter α on temperature for 2 kOe (▲), 5 kOe (○) and 10 kOe (●).

$$\frac{1}{\tau_{orb}} = \frac{1}{\tau_0} e^{-\frac{\Delta_{orb}}{kT}} \tag{4}$$

where k is the Boltzmann constant and Δ_{orb} is the separation of the ground from the excited state.

Data for seven values of the magnetic field in the 0.5–10 kOe range have been analyzed. Neither τ_0 nor Δ_{orb} exhibits any systematic dependence on the strength of the magnetic field. From the seven sets of data the mean value for τ_0 is $3.4(\pm0.8) \times 10^{-7}$ s, whereas the mean value for Δ_{orb} is $31(\pm1)$ cm^{-1}.

Clearly, the value of Δ_{orb} is too large to be related with a barrier pertinent to being within the ground state $S = 3/2$ manifold for which $\Delta_{3/2} \sim 0.18$ cm^{-1}. On the other hand, this energy might compare to the separation of the two doublet excited states from the quartet ground state. These $S = 1/2$ states are degenerate (in idealized D_{3h} symmetry, see below), lying at $\Delta = 3/2|J|$ above the ground $S = 3/2$ state. From the analysis of the temperature dependence of the magnetic susceptibility data within the exchange Hamiltonian (3), the value of $J_{ij} = -24$ cm^{-1} corresponds to a situation where the $S = 1/2$ excited states are at $\Delta = 36$ cm^{-1} above the ground $S = 3/2$ quartet (Fig. 8), which can be compared to $\Delta_{orb} = 31(\pm1)$ cm^{-1} given above. It is thus reasonable to assume that the observed relaxation behavior for $T > 4.5$ K involves transitions between the ground $S = 3/2$ and the excited $S = 1/2$ states. Relaxation involving two different spin manifolds has been observed in ferromagnetically coupled Cu(II) [25] and Ti(II) [26] pairs by magnetic resonance techniques and the ferromagnetic diferric

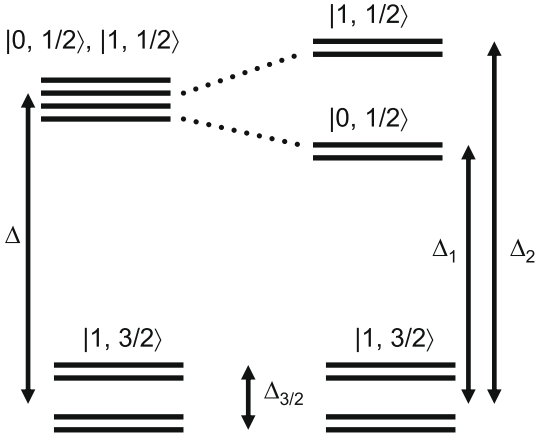

Fig. 8. Energy levels in zero field for the ferromagnetic Cu_3 cluster. The left panel corresponds to the equilateral and the right panel to the isosceles geometry. The labeling of the states is given according to the $|S'_{22}, S\rangle$ nomenclature (see text).

complex $[Et_4N]_3[Fe_2F_9]$ by *ac* susceptometry [27]. Recently, relaxation involving excited spin manifolds has been suggested by scrutinized *ac* susceptibility measurements in the case of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ derivatives [28].

The energy barrier Δ_{orb} deduced from the Orbach mechanism is of the same order of magnitude as the barrier Δ, calculated from the exchange coupling constant, J, of Eq. (3). We observe however that Δ_{orb} is $\sim 5\ cm^{-1}$ lower than Δ, this difference being greater than the experimental error. It would be worthwhile investigating the origin of this discrepancy. Below we discuss how the exchange coupling scheme may explain this difference.

For the analysis of the magnetic susceptibility data it has been assumed that the three exchange coupling constants in Eq. (4) are all equal ($J_{ij} = J$), corresponding to ideal D_{3h} symmetry (equilateral triangle). An inspection of the structure of **1** (Fig. 1) indicates that the triangle of the Cu(II) ions is isosceles rather than equilateral (i.e., it is described by Cu2, Cu2′ and Cu1). This suggests that (at least) one of the exchange coupling constants might be different: $J_{12} = J_{12'} = J_0 \neq J_{22'} = J'$.

Without loss of generality S_2 and $S_{2'}$ can be coupled to an intermediate spin $S_{22'} = 0$ or 1 and then to S_1 in order to obtain the (total) system spin S. Using the nomenclature $|S_{22'}, S\rangle$, the $S = 3/2$ state must have the form $|1, 3/2\rangle$, while the two $S = 1/2$ states have the forms $|0, 1/2\rangle$ and $|1, 1/2\rangle$ with energies $\Delta_1 = -\frac{1}{2}J_0 - J'$ and $\Delta_2 = -\frac{3}{2}J_0$ above the ground $|1, 3/2\rangle$ state, respectively. Because the Cu2–Cu2′ distance is longer than the other two within the trinuclear core of **1**, it is assumed that $|J'| < |J_0|$, yielding $\Delta_1 < \Delta_2$ (Fig. 8).

The lowering of the symmetry due to two different exchange coupling constants, J_0 and J', raises the degeneracy of the two $S = 1/2$ states. If small, the differentiation between J_0 and J' cannot be resolved in the analysis of the magnetic susceptibility vs T experimental data for which an equilateral model is sufficient. Within the equilateral model the deduced exchange coupling constant J represents an average value ($J = (2J_0 + J')/3$) and it reproduces accurately the average separation between the $S = 3/2$ and the $S = 1/2$ excited states with $\Delta = \frac{\Delta_2 + \Delta_1}{2}$.

In order to explore the effects of the involvement of two excited states in the relaxation process through an Orbach mechanism equation (4) is modified as follows:

$$\frac{1}{\tau_{orb}} = \frac{1}{\tau_{01}} e^{-\frac{\Delta - \delta}{kT}} + \frac{1}{\tau_{02}} e^{-\frac{\Delta + \delta}{kT}} \tag{5}$$

where $\delta = \frac{\Delta_2 - \Delta_1}{2}$.

For the pre-exponential factors [20]:

$$\frac{1}{\tau_{01,2}} = b_{1,2}(\Delta \mp \delta)^3 \tag{6}$$

The experimental $\ln \tau_{orb}$ vs $1/T$ data for the seven field values were fitted within the framework of Eqs. (5) and (6). For the fittings, Δ was kept at $36\ cm^{-1}$ and assumed further that $b_1 = b_2 = b$.

The obtained theoretical curves deviate little from linearity and they almost coincide with the straight lines deduced from a single Orbach mechanism (Fig. 5). However this apparent linear dependence acquires a different meaning: the Orbach relaxation mechanism involves two excited states with an average separation $\Delta = \frac{\Delta_2 + \Delta_1}{2} = 36\ cm^{-1}$ and $\delta = \frac{\Delta_2 - \Delta_1}{2} = 6.7(\pm 0.4)\ cm^{-1}$ from the ground state and not one excited state with $\Delta_{orb} = 31\ cm^{-1}$.

From the above discussion we conclude that involvement of the isosceles model offers an explanation for the apparent small difference between the value of a single Orbach energy barrier Δ_{orb} (Eq. (4)) and the value of Δ imposed by the exchange coupling scheme in the equilateral configuration (Eq. (3)). The combination of the temperature dependence of the magnetic susceptibility and the relaxation properties within the framework of the Orbach process may be used to unveil possible differentiation between the exchange coupling constants in the present Cu_3 complex. Alternatively, analysis of the relaxation properties of a PTMC with an Orbach process may imply more than one, close lying excited states. This is of particular importance in the case of PTMCs with larger nuclearity and spin of the individual ions and more complicated exchange coupling schemes than the present, relatively simple PTMC.

The mean value of δ implies $J_0 = -28.5(\pm 2.0)\ cm^{-1}$, $J' = -15.0(\pm 1.0)\ cm^{-1}$, whereas the mean value of parameter $b = 25(\pm 5)\ s^{-1}\ K^{-3}$, respectively. From Eq. (6) we obtain $\tau_{01} = 5.5(\pm 1.7) \times 10^{-7}$ s and $\tau_{02} = 1.8(\pm 0.5) \times 10^{-7}$ s. These values should be taken with caution and should be considered as order of magnitude estimates. In particular, in the preceding analysis $b_1 = b_2$ has been assumed. These parameters depend critically on the mixing between the $S = 3/2$ ground and $S = 1/2$ excited states resulting from the involvement of non-Heisenberg interactions such as dipolar, anisotropic and antisymmetric exchange [29–31]. The relation between b_1 and b_2 may be obtained by further analysis of the EPR spectra and will be presented elsewhere.

Finally, a brief report on the relaxation properties at $T < 4.5$ K follows. For $H_{DC} > 2.0$ kOe, the points (χ', χ'') still lie in a semicircle in the Cole–Cole plots. However, the analysis of the data requires a non-zero value for the inhomogeneity parameter α. As the temperature decreases, α increases, reaching a value of ~ 0.3 at 2.0 K (Fig. 7). This behavior suggests that under these conditions the system relaxes with a temperature dependent distribution of relaxation times [1]. A gradual increase of α as temperature decreases has been observed in 3d- [32,33] or 4f- [14] based SMMs. For lower magnetic fields (<2.0 kOe) the points (χ', χ'') do not lie on a semicircle, but the experimental curves have a rather irregular shape providing evidence for a multitude of relaxation processes. Such irregular shapes in the Cole–Cole plots were observed in the ferromagnetic diferric complex $[Et_4N]_3[Fe_2F_9]$ at low magnetic fields [27].

It is well known that at low temperatures the Orbach process becomes less efficient and other relaxation mechanisms such as the direct, Raman-like or phonon-bottleneck processes prevail [20]. Apart from direct interactions of the spin system with the lattice, interactions with the nuclear spins as well as inter-cluster interactions may also have a significant contribution especially at low fields. It is likely that all these processes contribute to the complicated temperature and field dependence of the relaxation properties of **1** at $T < 4.5$ K.

4. Summary

In the present work we have reported *ac* susceptibility studies in the presence of external magnetic fields for a triangular Cu_3 ferromagnetic cluster. In the 4.5–8 K temperature range the relaxation follows the Orbach mechanism involving transitions between the ground $S = 3/2$ and excited $S = 1/2$ states. The analysis suggests that the magnetic properties of the system are better described assuming two different rather than three equal exchange coupling constants (i.e., isosceles rather than equilateral triangle). Below 4.5 K the relaxation involves different mechanisms depending on the external magnetic field.

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