dure described previously [8,21]. Electrochemical oxidation of Al was carried out in 0.3 M $H_2C_2O_4$ solution (40 V, 17 °C, pore density of up to 1.1×10^{10} cm^{-2}) and 10 wt.-% H_3PO_4 solution (160 V, –3 °C, pore density of up to 7×10^8 cm^{-2}) with graphite as counter electrode. As-prepared AAO was separated from Al by voltage reduction and chemically etched with 5 wt.-% H_3PO_4 solution at room temperature for about 30 min to give a through-hole AAO membrane.

Electroplating of Metallic Nanostructure: To set up the simple two-electrode system, a Au base electrode was plasma-sputtered on one side of the AAO membrane to a thickness of 150–200 nm and covered with an indium tin oxide (ITO)-coated glass substrate, thus avoiding unwanted metal plating on the sputtered Au surface. A large-area Pt wire, graphite, and stainless steel were used as the counter electrode for Pt, Ni, and Au plating solutions, respectively. Electroplating solutions are commercially available (Pt: Technic platinum AP solution; Au: Technic Orosene 999) or easily prepared (Ni: $NiCl_2 \cdot 6H_2O$, $Ni(H_2NSO_3)_2 \cdot 4H_2O$, H_3BO_3 and buffer solution of pH 3.4). The power supply was a Keithley 2400 Source Meter and controlled by a custom-written LabView program. The hole size of the spacer in contact with the plating solution was 6.0 mm, giving an AAO surface area of 0.28 cm^2. The area density of nanochannels on the AAO surface was calculated to lie in the range of 50–60 % and the measured current value during the electroplating was in the range of 40–50 mA. Therefore, the value of the actual current density of our electroplating condition can be calculated as 200–300 mA/cm^2.

Characterization of Metallic Nanostructured Material: Metal nanostructures prepared within AAO channels were characterized by optical microscopy (Carl Zeiss AXIOTECH), TEM (Philips CM-20 and Hitachi 7600), HRTEM (JEM-3000F), FE-SEM (JEOL JSM-6700F), and EDX spectrometry (EDAX falcon and Oxford).

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# Resonant Quantum Tunneling in a New Tetranuclear Iron(III)-Based Single-Molecule Magnet**

By *María Moragues-Cánovas, Éric Rivière, Louis Ricard, Carley Paulsen, Wolfgang Wernsdorfer, Gopalan Rajaraman, Euan K. Brechin,* and *Talal Mallah**

One of the challenges in molecular magnetism is the preparation of molecular clusters that behave as single-molecule magnets (SMMs).[1] Such behavior, due to the slow relaxation of the magnetization below a given temperature, may open new horizons for one-molecule information storage—even though not above liquid-helium temperature for the time being. The number of polynuclear complexes that behave as SMMs is increasing and examples of V, Mn, Fe, Ni, and Co complexes can be found in the literature.[2] But to date, SMMs based on iron(III) are still rare.

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Two important issues can be addressed. The first one concerns understanding of the electronic factors that govern the magnetic anisotropy that is at the origin of the blocking of the magnetization, since the deviation from pure axial anisotropy induces the quantum tunneling of the magnetization.[2] This tunneling leads to a faster relaxation, which may destroy the magnet-like behavior of the molecules. On the other hand, intermolecular interactions may have a dramatic effect on the magnetic behavior, as was recently shown.[3] The second issue is synthetic. Two approaches, i.e., rational and serendipitous assembly have been explored in order to obtain large magnetic clusters. Even though the rational approach allows the preparation of bimetallic systems, the clusters behave as SMMs in very few cases.[4] SMM behavior has mainly been observed in polynuclear complexes obtained by a one-pot reaction, however, since serendipity plays a fundamental role, the structure of the resulting clusters is difficult to predict.[5] One of the main requirements to succeed in producing polynuclear complexes with such an approach is to use what are called "flexible" ligands.[5a,6] Such ligands must be able to act simultaneously as bridging and terminal ligands towards metal ions. Carboxylate and pyridonate ligands, among others, are the best examples. Recently, 1,1,1-tris(hydroxymethyl)ethane (H_3thme; shown below) showed its ability to stabilize large polynuclear complexes.[7] Depending on its degree of deprotonation this ligand can be bridging and/or terminal.
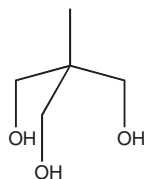
In this communication, we report the preparation, magnetic studies, and SMM behavior of a novel tetranuclear iron(III) complex, formula $Fe_4(thme)_2(C_3H_7OH)_6Cl_6$.

The structure of the complex[8] consists of a central Fe atom connected to three peripheral Fe atoms through two fully deprotonated thme ligands, which occupy the apical positions of the Fe_4 skeleton (Fig. 1). Two propanol molecules in *trans* position and two Cl atoms in *cis* position complete the coordination sphere of the peripheral Fe atoms. The molecule has a principal C_2 symmetry axis along the central and
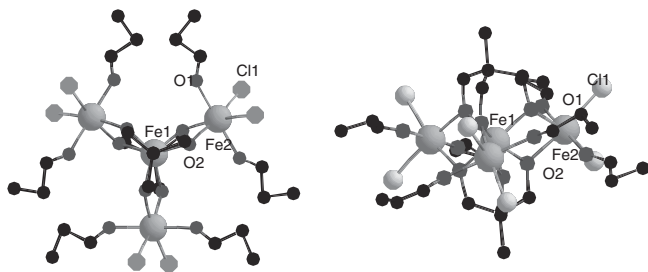
Figure 1. View of the molecular structure of the tetranuclear Fe_4 complex along the pseudo C_3 axis. Hydrogen atoms were removed for clarity.

one of the peripheral Fe atoms. All the molecules have their principal axes along the *b* direction of the crystal. The Fe–O–Fe angles are almost identical and vary between 105.0(2) and 105.3(2)°. The intramolecular $Fe_{central}$–$Fe_{peripheral}$ distances are the same (3.157(4) Å). No H bonds are present, however there are relatively short intermolecular Cl–Cl distances (5.4 Å) leading to a three-dimensional (3D) network with very short Fe–Fe intermolecular distances of 8.2 Å. A similar Fe_4 complex has already been reported by Gatteschi and coworkers.[2f,9,10]

Magnetic studies were performed using a superconducting quantum interference device (SQUID) magnetometer in the 300–2 K temperature range with an applied field of 500 G for susceptibility, χ_M, and between 0 and 5.5 T at 2 K, 4 K, and 6 K for magnetization measurements. The $\chi_M T = f(T)$ plot (Fig. 2) has a minimum at $T = 198$ K, indicating the presence of intramolecular antiferromagnetic interaction. A ground state $S = 5$ is thus expected due to the antiferromagnetic cou-
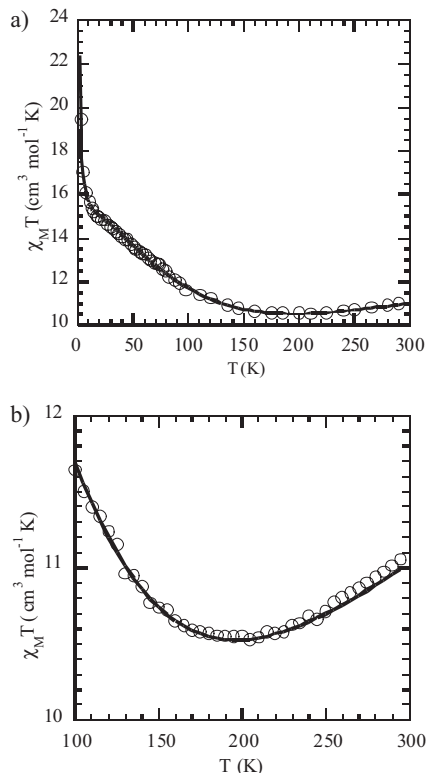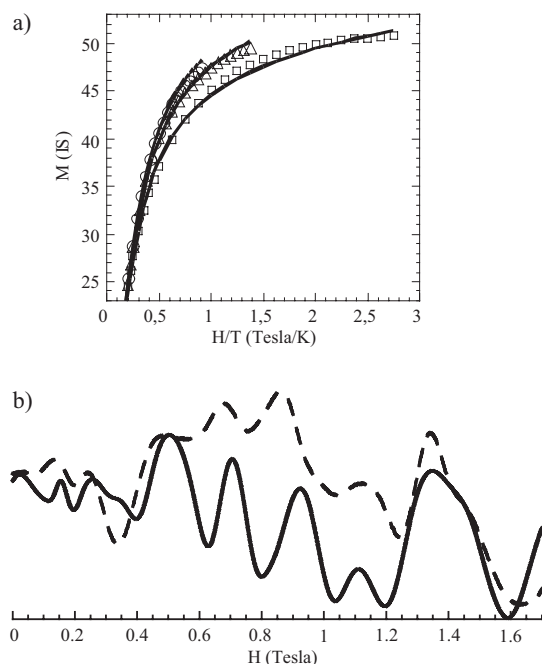

Figure 2. a) $\chi_M T = f(T)$ with $H = 500$ Oe. b) Enlarged view of the 100–300 K range.

pling between the central and the peripheral iron ions. Below $T = 15$ K, $\chi_M T$ increases to a maximum value of 22.06 $cm^3 mol^{-1}$ K at $T = 2$ K, higher than expected for a $S = 5$ ground state (15 $cm^3 mol^{-1}$ K assuming a *g*-value equal to two). This may indicate the occurrence of a weak ferromagnetic coupling between the clusters at low temperature. The experimental data in the range 2–300 K were fitted to the the-

oretical expression corresponding to the following spin Hamiltonian

$$\mathscr{H} = -JS_{Fe_1}(S_{Fe_2} + S_{Fe_3} + S_{Fe_4}) + g\beta HS \qquad (1)$$

including a term (zj) that takes into account the intermolecular interactions in the framework of the molecular field approach. J is the exchange-coupling parameter between the central Fe_1 and the three peripheral Fe_2, Fe_3, and Fe_4 atoms, S_{Fei} are the local spin operators, S is the total spin ($S = S_{Fe_1} + S_{Fe_2} + S_{Fe_3} + S_{Fe_4}$), g the average g value, β the Bohr magneton, and H the applied magnetic field. The fit of the experimental data leads the to following parameters: $J = -28.2$ cm^{-1}, $g = 1.97$, $zj = +0.05$ cm^{-1} with an agreement factor $R = 5 \times 10^{-5}$. This corresponds well to a spin ground state $S = 5$ separated by 70.5 cm^{-1} from the first $S = 4$ excited states with weak intermolecular ferromagnetic interaction. The magnetization, M, versus the applied magnetic field, H, was measured at 2 K, 4 K, and 6 K. The $M = f(H/T)$ plots (Fig. 3) show the presence of an appreciable magnetic anisotropy within the $S = 5$ ground state. A reasonable fit considering only the ground state popu-
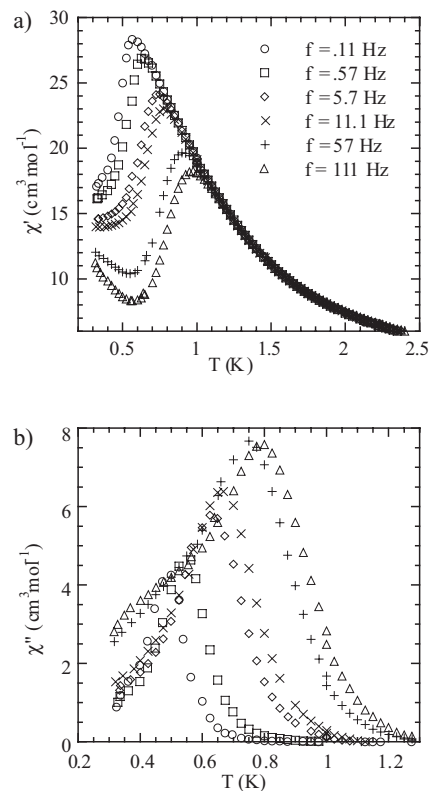
data leads to D and E values equal to -0.33 and 0.006 cm^{-1}, respectively with an isotropic g-value taken to be equal to 2.03 (Fig. 3b).[11] Introducing the rhombic parameter E is necessary to reproduce all the features of the EPR spectrum. The presence of an appreciable axial anisotropy and very small rhombic contribution within the $S = 5$ ground state together with a large separation of the first excited states suggest the possibility of SMM behavior and quantum tunneling of the magnetization.

Alternating current (ac) susceptibility measurements were performed at different frequencies, f, of the oscillating field in zero direct current (dc) field. A maximum is observed for the in-phase response at $T = 0.97$ K for $f = 111$ Hz. On decreasing the frequency of the oscillating magnetic field, the temperature of the maximum shifts down to around 0.5 K for $f = 0.11$ Hz (Fig. 4). A frequency-dependent out-of-phase signal is associated to the in-phase one below $T = 1$ K, suggesting a blocking of the magnetization below 1 K (Fig. 4b). To confirm the SMM behavior, magnetization measurements were

Figure 3. a) $M = f(H/T)$ at $T = 2$ ($\square$), 4 ($\triangle$), and 6 ($\bigcirc$) K. The solid lines correspond to the best fit (see text). b) The experimental Q band EPR spectrum ($\cdots$) at $T = 5$ K and the fit (–) for $S = 5$, $D = -0.33$ cm^{-1}, $E = 0.006$ cm^{-1}, and $g_x = g_y = g_z = 2.03$.

Figure 4. a) $\chi' = f(T)$ at different frequencies f of the oscillating field in dc zero field. b) The $\chi'' = f(T)$ plots at the same frequencies.

lated, and neglecting the intermolecular interaction, leads to $D = -0.32$ cm^{-1}, $E = 0$, and $g = 1.98$, where D and E are the axial and the rhombic anisotropy parameters respectively. The sign and the order of magnitude of D were confirmed by the Q-band electron paramagnetic resonance (EPR) spectrum performed in the field range 0–1.7 T at $T = 5$ K. The fit of the

performed on a single crystal coupled to a micro-SQUID loop.[12] The measurements were made with the magnetic field parallel to the easy axis of the crystal. Hysteresis loops were observed below 1 K with coercivities increasing upon decreasing temperature (Fig. 5a). This behavior is due to the fact that the relaxation time becomes slower upon cooling, as expected
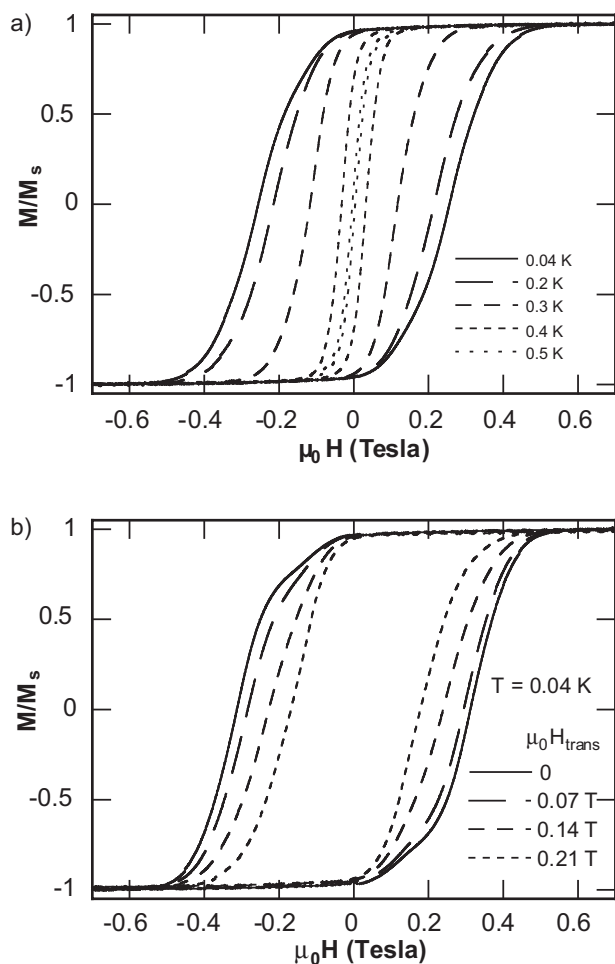
Figure 5. a) Hysteresis loops of a single crystal with the magnetic dc field parallel to the easy axis at different temperatures; b) hysteresis loops at $T = 0.04$ K with dc field parallel to the easy axis in the presence of different values of the transverse field.

for a SMM. No clear step-like features indicative of quantum tunneling of the magnetization are present. However, a smooth step can be seen in the hysteresis loop between $H = 0$ and -0.2 T (or 0.2 T) at $T = 0.04$ K, which may indicate that the steps were smeared out by intermolecular interactions. Indeed, the plot of the $1/\chi'$ versus temperature between $T = 1$ K and 3 K gives a straight line (not shown here) that leads to a positive Weiss constant of 0.5 K confirming the presence of weak intermolecular ferromagnetic interaction (this confirms the $\chi_M T$ behavior between 15 K and 2 K). The relatively short distances between the chloride atoms belonging to different tetranuclear complexes (see above) may be at the origin of the weak intermolecular ferromagnetic interaction observed. In order to check the presence of quantum tunneling of the magnetization (QTM), the temperature was set at $T = 0.04$ K and a transverse field (perpendicular to the easy axis) was applied to the crystal. Figure 5b shows that the coercivity decreases upon increasing the magnitude of the transverse field, which is considered as an indication of an en-

hancement of the relaxation time. Indeed, the transverse field couples the different M_S sub-levels of the $S = 5$ ground state, increasing the relaxation time by the tunneling mechanism (since the temperature is very low) and thus reducing the width of the $M = f(H)$ plots. One of the best evidences for the existence of QTM is the measure of the relaxation time at different temperatures. Two regimes occur: one is temperature dependent between 0.6 K and 0.4 K and the other is temperature independent when approaching $T = 0.04$ K (Fig. 6). The fit of the relaxation time τ versus $1/T$ plot, taking into account the results of the out-of-phase susceptibility data and the relaxation studies done on the single crystal by micro-SQUID,
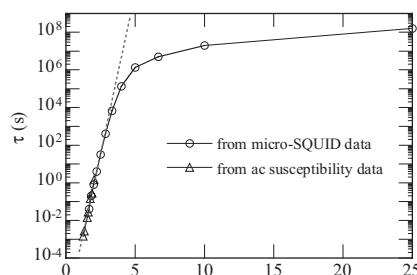
Figure 6. Relaxation time (τ) versus $1/T$. The dashed line corresponds to the fit of the high-temperature region showing an Arrhenius-type behavior.

shows a thermally activated process between $T = 1$ K and 0.4 K of the Arrhenius type ($\tau = \tau_0 \exp(-E_a/kT)$) with $\tau_0 = 3.7 \times 10^{-8}$ s and an anisotropy barrier $E_a/k = 8.5$ K. The τ_0 value is in the range expected for other SMMs.[2b,13] Below $T = 0.3$ K, the relaxation of the magnetization is not thermally activated anymore and becomes temperature independent at $T = 0.04$ K, indicating the occurrence of resonant quantum tunneling within the $S = 5$ ground state. The anisotropy barrier is weaker than that calculated from DS^2 (11.5 K), where S is the spin of the ground state and D the zero-field splitting parameter extracted from the EPR data. The weaker D value is due to the fact that the anisotropy is not purely axial; a weak transverse contribution ($E \neq 0$) is present, which reduces the magnitude of the barrier and is responsible for the tunneling process.

In this communication, we have demonstrated that the tetranuclear Fe$_4$ complex shows SMM behavior with quantum tunneling of the magnetization within the ground state. However, the presence of intermolecular interactions precludes the observation of sharp steps in the magnetization versus field plots. This is an interesting example showing the complete difference in the dynamic of the reversal of the magnetization in comparison to the Fe$_4$ complex already reported, where sharp steps corresponding to frank tunneling processes are observed.[10] From the synthetic point of view, this complex is interesting. Its preparation requires the crystallization of the powder after redissolving it in a mixture of tetrahydrofuran (THF) and 2-propanol (see Experimental). We have been able to change the nature of the alcohol and prepare

complexes with 1-propanol and ethanol, for instance, without disturbing the metallic skeleton. The preparation of other complexes with different alcohols (bulky ones) is underway in order to study the effect of intermolecular interactions on the quantum tunneling behavior in a series of similar complexes.

Experimental

Synthetic Procedure: Solid 1,1,1-tris(hydroxymethyl)ethane (thme), (246 mg, 2.0×10^{-3} mol) and $NaOCH_3$ (333 mg, 6.2×10^{-3} mol) were added to a solution of $FeCl_3$ (1 g, 6.16×10^{-3} mol) in methanol (25 mL), and the mixture was stirred at room temperature for 24 h. The resulting solution was filtered and the solvent removed under vacuum. The orange precipitate obtained was redissolved in 25 mL of THF/2-propanol (1:1). Red plates were obtained within one week in 50–55 % yield by slow evaporation of the resulting solution. The crystals are stable at room temperature and no loss of propanol is observed. Anal. Calcd for $C_{28}H_{74}Cl_6Fe_4O_{12}$: C, 32.37; H, 7.12. Found: C, 32.48; H, 7.21.

Magnetic Studies: The magnetic studies were carried out on ground single crystals obtained from the same sample batch for which the single crystal was selected for structural determination. Two SQUID magnetometers were used for dc and ac measurements operating in the temperature ranges 300–2 and 3–0.5 K, respectively. The measurements on an oriented single crystal were performed using an array of micro-SQUIDs arranged on a substrate (see [12]) operating between 1 and 0.04 K and a dc magnetic field up to 1.7 T.

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[8] Crystallographic data: $C_{28}H_{74}Cl_6Fe_4O_{12}$, $M = 1038.97$, monoclinic, $a = 23.624(2)$ Å, $b = 13.639(2)$ Å, $c = 16.394(2)$ Å, $\beta = 118.710(2)$, $U = 4632.9(10)$ Å^3, $T = 150$ K, space group $C2/c$, $Z = 4$, ((Mo-K(α1) = 0.71069 Å, 12218 reflections measured, of which 5283 were unique ($R_{int} = 0.0251$). The final conventional R-factor [based on F and 3961 data with $F > 4(F)$] was 0.0894. The structure was solved by direct methods (SHELXS97) and refined with SHELXL97. See: A. Altomare, G. Cascarano, Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343; G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany **1998**.

[9] The skeleton of the two complexes is the same with very similar Fe–O distances and Fe–O–Fe angles However, in the present case two thme⁻ bridge the four Fe atoms instead of six methoxo groups. Furthermore, the coordination sphere of the peripheral Fe atoms is different because of the presence of two Cl and two 2-propanol entities in the present case, as opposed to the two dipivaloylmethane anions in the already reported complex. This leads to different Fe$_{peripheral}$–X distances and Fe–X–Fe angles. This may have an important influence on the local anisotropy parameters and thus on the overall D value of the $S = 5$ ground state. Another important difference is the intermolecular interaction mediated by the Cl atoms and the presence of intermolecular Fe–Fe distances of 8.2 Å in the present compound, while such distances are larger than 9 Å in the already reported compound.

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[11] The magnetization and the EPR data were fitted considering negative and positive D values. The best fits were obtained only in the case of a negative D value.

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