Multifaceted magnetization dynamics in the mononuclear complex [ReIVCl4(CN)2]2-

Feng, Xiaowen; Liu, Jun-Liang; Pedersen, Kasper S.; Nehrkorn, Joscha; Schnegg, Alexander; Holldack, Karsten; Bendix, Jesper; Sigrist, Marc; Mutka, Hannu; Samohvalov, Dumitru; Aguilà, David; Tong, Ming-Liang; Long, Jeffrey R.; Clérac, Rodolphe

Published in:
Chemical Communications

DOI:
10.1039/c6cc05473k

Publication date:
2016

Document version
Publisher's PDF, also known as Version of record

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Citation for published version (APA):
The mononuclear complex (Bu₄N)₂[Re⁴⁺Cl₄(CN)₂]·2DMA (DMA = N,N-dimethylacetamide) displays intricate magnetization dynamics, implying Orbach, direct, and Raman-type relaxation processes. The Orbach relaxation process is characterized by an energy barrier of 39 K (27 cm⁻¹) that is discussed based on high-field electron paramagnetic resonance (EPR), inelastic neutron scattering and frequency-domain THz EPR investigations.

For paramagnetic molecules with a spin ground state of $S_T$, the presence of anisotropy may result in a magnetic bistability through a near-orbitally degenerate ground state, which is separated by an energy barrier, $\Delta$, thereby leading to slow dynamics of the magnetization. As a family, such molecules are referred to as single-molecule magnets (SMMs). Although the first generations of SMMs were polynuclear complexes characterized by ever larger spin ground states, theoretical and experimental results have established that an increase in the spin ground state is compensated by a corresponding decrease in total magnetic anisotropy. To overcome this problem, new approaches have emerged, such as using molecules containing a single paramagnetic lanthanide or actinide ion, both known for their often pronounced magnetic anisotropy. The effective energy barriers for magnetization reversal, $\Delta_eff$, for these molecules have been reported to exceed 1000 K (695 cm⁻¹), which is an order of magnitude larger than the original Mn₁₂ SMM.

More recently, it was shown that mononuclear first-row transition metal complexes can display significant magnetic anisotropy, originating from a near-orbitally degenerate ground state where the orbital angular momentum is left unquenched. Moreover, taking advantage of the Kramers theorem, fast quantum tunneling could be effectively avoided by using half-integer spin metal ions. Following this strategy, several mononuclear SMMs based on first-row transition metal ions were reported. For example, a recent linear two-coordinate Fe知识产权 complex displayed a $\Delta_eff$ of 354 K (246 cm⁻¹), and a magnetic hysteresis up to 6.5 K, thereby challenging high-performing lanthanide systems. In addition to the synthetic challenges of generating such low-coordinate complexes, mononuclear SMMs of first-row transition metal ions have the intrinsic disadvantage of possessing weak spin–orbit coupling and thus may have a relatively small magnetic anisotropy. To meet this challenge, recent attention turned to 5d metal ions, for which strong spin–orbit coupling can be combined with the tunability of the electronic structure through the chemically controllable geometry and ligand field.

Although SMM behavior seemed to be reserved for systems with $D < 0$ (easy-axis type anisotropy; with $\hat{H} = D\hat{S}_z^2$), an increasing number of complexes featuring $D > 0$ (easy-plane type anisotropy) in conjunction with SMM properties have been reported. However, for molecules with half-integer spin, a doubly degenerate ground state is always assured by the Kramers theorem, regardless of the sign of $D$. Thus, in principle, observation of slow magnetization dynamics via an Orbach process involving at least three $M_T$ microstates is always possible for a half-integer spin...
Fig. 1 (a) Structure of the trans-[ReIVCl4(CN)2]2− complex obtained from single-crystal X-ray diffraction on 1 at 50 K. (b) Energy level diagram calculated from the previously determined D and E parameters.\textsuperscript{15}\textsuperscript{a} The blue shading is a schematic representation of the acoustic phonon density with the cut-off at the Debye temperature. The arrows indicate the direct (blue), Raman (grey), and Orbach (green) relaxation pathways from state |KD\textsubscript{1}\rangle to |KD\textsubscript{2}\rangle (the diagram is symmetrical for the reverse processes). The magnetic moment, μ\textsubscript{B}, is defined as μ\textsubscript{B} = g\textsubscript{eff}μ\textsubscript{B}/2, where g\textsubscript{eff} is the g-factor treating the two doublets as effective spin 1/2. The virtual state, relevant for the Raman process, is placed pictorially at an arbitrary energy with an arbitrary magnetic moment.

Recently, rhenium(IV) complexes (Bu\textsubscript{4}N)\textsubscript{2}[Re(ox)X\textsubscript{4}](ox = oxalate, X = Cl, Br), (PPh\textsubscript{3})\textsubscript{2}[ReF\textsubscript{6}]2H\textsubscript{2}O and Zn(viz)\textsubscript{2}[ReF\textsubscript{6}] (viz = 1-vinylimidazole) were shown to display slow relaxation of the magnetization, the relaxation time was extracted from the experimentally accessible time window. Upon applying small static fields, H, however, clear frequency- and temperature-dependent ac signals were observed (Fig. 2 and Fig. S1, ESI\textsuperscript{†}). To elucidate the effect of the applied magnetic field on the slow relaxation of magnetization, the relaxation time was extracted from the variable-field and variable-temperature ac susceptibility data (\tilde{\chi}(T, H); Fig. 3 and Fig. S1–S6, ESI\textsuperscript{†}) by fitting the experimental data to the generalized Debye model. The relaxation time at 1.9 K monotonically decreases with increasing magnetic field (Fig. 3b). This behavior is expected for a direct process of relaxation, which involves only the two components of the lowest-lying Kramers doublet and is accelerated upon increasing magnetic field (in accordance with the first term in eqn (2)).\textsuperscript{13,16} In the low field regime (μ\textsubscript{B}H ≪ k\textsubscript{B}T), other processes (Orbach, Raman, etc.) we hereby report the observation of a slow relaxation of the magnetization for 1 that is reminiscent of SMM behavior, and discuss its possible origins. In 1, the rhenium(IV) center of the [ReCl\textsubscript{4}(CN)\textsubscript{2}]\textsuperscript{3−} complex anion resides in an approximate D\textsubscript{4h} symmetric environment\textsuperscript{15} and close inspection of the X-ray crystal structures at 50 and 139 K reveals only small differences in the local coordination environment of the metal ion. As expected for typical thermal contraction, the bond distances shrink slightly with decreasing temperature. The Re–Cl distances are 2.331(1) and 2.341(1) Å at 139 K, while at 50 K, these distances are 2.321(2) and 2.334(2) Å, respectively. Selected interatomic distances and bond angles for 1 are listed in Table S1 (ESI\textsuperscript{†}).

Alternating current (ac) magnetic susceptibility measurements were performed to detect any slow relaxation of the magnetization in a polycrystalline sample of 1. In the absence of a static magnetic field, the relaxation time is too short to be observed in the experimentally accessible time window. Upon applying small static fields, H, however, clear frequency- and temperature-dependent ac signals were observed (Fig. 2 and Fig. S1, ESI\textsuperscript{†}) by fitting the experimental data to the generalized Debye model. The relaxation time at 1.9 K monotonically decreases with increasing magnetic field (Fig. 3b). This behavior is expected for a direct process of relaxation, which involves only the two components of the lowest-lying Kramers doublet and is accelerated upon increasing magnetic field (in accordance with the first term in eqn (2)).\textsuperscript{13,16} In the low field regime (μ\textsubscript{B}H ≪ k\textsubscript{B}T), other processes (Orbach, Raman, etc.)

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Fig. 2 Frequency dependence of the in-phase (χ′, top) and out-of-phase (χ″, bottom) components of the ac magnetic susceptibility at different temperatures for a polycrystalline sample of 1 under a 2000 Oe dc field. The solid lines are the best fits to the generalized Debye model.
governing magnetization relaxation are only weakly field dependent and thus their contributions to the relaxation time have been assumed to be constant, $k(T)$, as in eqn (2).

$$\tau(H)^{-1} = AH^4T + k(T)$$

(2)

Note that upon increasing the dc field, the probability of magnetization relaxation by quantum tunneling should be suppressed, thereby resulting in a slowing down of the relaxation. This effect is not experimentally observed for 1, and quantum tunnelling has thus not been considered in the modeling of its relaxation properties.\(^{16,19,20}\)

In order to reproduce the temperature dependence of the relaxation time, Orbach and/or Raman processes should be considered in addition to the direct process already evidenced in the field dependence (vide supra).\(^{17-21,22}\) Accordingly, two simple parameter-sparse models were considered, as given in eqn (3) and (4). These two approaches incorporate the contributions from both direct and Raman processes (eqn (3)) and both direct and Orbach processes (eqn (4)), with the fixed parameter $A = 3.0 \times 10^4 \, \text{s}^{-1} \, \text{K}^{-1} \, \text{T}^{-4}$ extracted from the $\tau(1.9 \, \text{K}, H)$ data.

$$\tau(T)^{-1} = AH^4T + CT^n$$

(3)

$$\tau(T)^{-1} = AH^4T + \tau_0^{-1}\exp[-A_{\text{eff}}/(k_B T)]$$

(4)

Although the fit with eqn (3) is in good agreement with the experimental data (Fig. S7, ESI†), the Raman exponent, $n$, reaches a suspiciously large value of $12 \pm 1$, which significantly exceeds the expected value of $n = 9$ for a Kramers system.\(^{21}\) Nevertheless, it should be noted that examples of $n > 9$ have been reported previously.\(^{23}\) These results were later attributed to the presence of a particular energy level structure where the energy of the first excited state, $J$, was close to, but larger than, the Debye temperature of the lattice (see Fig. 1b; in the present case, the Debye approximation is here justified by the low energy of the first excited state).\(^{24}\)

In this case, the Raman expression for $\tau(T)^{-1}$ is given by eqn (5).

$$\tau(T)^{-1} = C \left( T^9 + 180 \left( \frac{k_B}{A} \right)^2 T^{11} + 3240 \left( \frac{k_B}{A} \right)^4 T^{13} + \ldots \right)$$

(5)

For 1 with $A/k_B = 35 \, \text{K} \, (25 \, \text{cm}^{-1})$, the prefactors of the $T^{11}$ and $T^{13}$ terms amount to only $0.15 \, \text{K}^{-2}$ and $2.2 \times 10^{-3} \, \text{K}^{-4}$, respectively, indeed indicating an expected dominant $T^9$ behavior in the measured temperature window. On the other hand, the model containing an Orbach process (eqn (4)), which necessitates $A$ to be equal to or lower than the Debye temperature,\(^{25}\) is also insufficient to reproduce the experimental relaxation time (Fig. S8, ESI†). Furthermore, the calculated parameter $k$ ($154 \, \text{s}^{-1} \, \text{at} \, 1.9 \, \text{K}$) obtained from the fitting parameters of eqn (4) is in disagreement with the one obtained from eqn (2) and the field-dependence of the relaxation time ($k = 226 \, \text{s}^{-1}$ at 1.9 K). The disagreement between these models strongly suggests the presence of more than two types of relaxation processes in 1. Consequently, the direct, Raman and Orbach processes were all included in the fitting model given by eqn (6).

$$\tau(T,H)^{-1} = AH^4T + CT^n + \tau_0^{-1}\exp[-A_{\text{eff}}/(k_B T)]$$

(6)

In order to improve the reliability of the model, the complete experimental set of relaxation time data as a function of both field and temperature, $\tau(T,H)$, was fitted simultaneously using eqn (6). The resulting fit provided good agreement with all data, as depicted graphically with the solid lines in Fig. 3, and afforded $A = 2.9 \times 10^4 \, \text{s}^{-1} \, \text{K}^{-1} \, \text{T}^{-4}$, $C = 2.5 \, \text{s}^{-1} \, \text{K}^{-6.9}$, $n = 6.9$, $\tau_0 = 5.7 \times 10^{-11} \, \text{s}$, and $A_{\text{eff}}/k_B = 39 \, \text{K} \, (27 \, \text{cm}^{-1})$. This result supports the relevance of direct, Raman and Orbach processes for the magnetization dynamics of 1 in the temperature (Fig. S9, ESI†) and magnetic field ranges investigated. Considering the two Kramers doublets, KD\(_1\) and KD\(_2\) discussed above, the transverse anisotropy (eqn (1)) and the nonvanishing integral terms amount to only $0.15 \, \text{K}^{-2}$.

**Fig. 3** Relaxation time (1) versus (a) the inverse temperature ($T^{-1}$) at $H = 1, 2$ and 4 kOe and versus (b) the applied dc field at 1.9 K up to 10 kOe for 1. The solid lines are the best fits as described in the text.
multifaceted magnetization dynamics observed in the mononuclear complex salt \([\text{Bu}_4\text{N}]_2[\text{Re}^{VI}\text{Cl}_5(\text{CN})_2]2\text{DMA}\). Whilst this multi-parameter description of \(\tau(T,H)\) was only satisfactory after introduction of the Orbach mechanism, the lack of observation of the relevant excited state by spectroscopic techniques brings justified doubts on the presence of an operative Orbach relaxation in 1. This original example highlights the complexity of describing paramagnetic relaxation in molecular systems. Even if these elaborate multi-mechanism models for describing the relaxation phenomena are now becoming fashionable in the field of molecular magnetism, the combination of a large number of parameters with relatively uncharacteristic \(\tau(T,H)\) data in a narrow temperature interval may lead to questionable conclusions.

This work was supported by the National Science Foundation (NSF) under Grant CHE-1464841, the CNRS (PIC No. 06485), the University of Bordeaux, the Conseil Regional d’Aquitaine, the ANR, the French Embassy in the US (Chateaubriand fellowship for X. F.), the GdR MCM-2 and Sun Yat-Sen University (the International Program of Project 985 for J.-L. L.). K. S. P. thanks the Danish Research Council for Independent Research for a DFF-Sapere Aude Research Talent grant (4090-0201). The low temperature crystal structure was collected at the Stanford Nano Shared Facilities (SNSF), supported by the NSF under award ECSS-1542152. We thank also Philip C. Bunting for helpful discussions.

Notes and references


