Smooth transition between SMM and SCM-type slow relaxing dynamics for a 1-D assemblage of $\{Dy(nitronyl nitroxide)_2\}$ units[†]

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A model example for size effects on the dynamic susceptibility behavior is provided by the chain compound [{Dy(hfac)₃NitPhIm₂}Dy(hfac)₃] (NitPhIm = 2-[4-(1-imidazole)-phenyl]nitronyl nitroxide radical). The Arrhenius plot reveals two relaxation regimes attributed to SMM ($\Delta = 17.1$ K and $\tau_0 = 17.5 \times 10^{-6}$ s) and SCM ($\Delta = 82.7$ K and $\tau_0 = 8.8 \times 10^{-8}$ s) behaviors. The ferromagnetic exchange among the spin carriers has been established for the corresponding Gd derivative.

Low dimensional molecule-based magnetic systems attract a renewed interest since it has been shown that they may exhibit slow dynamics for the relaxation of their magnetization.^{1,2} Such materials known as single molecule magnets (SMMs) and single chain magnets (SCMs) not only permitted the observation of fascinating quantum phenomena³ but they are also investigated as potential candidates for future highdensity data storage materials.⁴ The 1-D systems are especially promising because of their virtual infinite spin ground state and intrinsic structural anisotropy.^{5,6} Among the various chemical routes investigated to obtain and improve the characteristics of those compounds, a strategy involving metal ions with organic radicals as ligands has proven very successful.^{7,8} For instance with anisotropic Ln ions a family of SCMs with different relaxation features could be obtained.⁹ For this series but in general for SCMs, the one-dimensional systems are not perfect and the actual material comprises spin chains of various lengths. As a result the signature for finite size effects is often detected by a crossover between two regimes in the dynamics of the relaxation of the magnetization in the lower temperature domain.¹⁰⁻¹² Here we report on a compound formed by $\{Dy(Nit)_2\}$ units (Nit stands for nitronyl nitroxide radical) assembled in a chain by the means of an additional Ln for which the AC magnetic susceptibility revealed two limit regimes in accordance with a SMM and a SCM, respectively. The transition between the two regimes is smooth with AC susceptibility features characteristic for a size distribution of the spin system. The homologous Gd compound shows that ferromagnetic interactions are operative between the Ln ion and the radical ligands, and between the $\{Ln(Nit)_2\}$ units and the further Ln ions bridging the units. The single-crystal X-ray structures and magnetic behaviors for the two 1-D compounds are described.

Reaction of 2-[4-(1-imidazole)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NitPhIm) radical with $Ln(hfac)_3$ (hfac = hexafluoroacetyl acetonate) yielded deep blue platelike crystals of [{ $Ln(hfac)_3$ }_2(NITPhIm)_2] 1 (Gd) and 2 (Dy).

Single-crystal X-ray diffraction analyses reveal that complexes 1 and 2 are isomorphous (see ESI⁺). Therefore, only the structure of complex 1 will be briefly described. As shown in Fig. 1, there are two independent Gd atoms in the asymmetric unit. Their coordination spheres comprise two oxygen atoms from two nitroxide groups for Gd(1) and two nitrogen atoms from two imidazole rings for Gd(2), and are completed to eight by the oxygen atoms of three didentate hfac ligands. The bond lengths are comparable to those of the reported Gd complexes with nitronyl nitroxides.¹³⁻¹⁵ Each NitPhIm acts as bridging ligand and is coordinated to two different Gd atoms through the oxygen atom of the nitronyl nitroxide group and the nitrogen atom of the imidazole ring to develop an one-dimensional chain having a 'head-to-head' motif. The $Gd(1) \cdots Gd(2)$ distance is 10.032 Å and the shortest interchain Gd...Gd separation is 10.199 Å.

The variable-temperature magnetic susceptibilities for 1 and 2 were measured from 300 to 2.0 K in an applied field of 1 kOe. The powder from crushed crystals of 2 was dispersed in grease to avoid orientation in the field. The $\chi_M T vs. T$ plots are shown in Fig. 2. At 300 K, the $\chi_M T$ value for 1 is 16.64 cm³ mol⁻¹ K, which is consistent with the expected value of 16.51 cm³ mol⁻¹ K for the isolated spins two $S_{Gd1} = S_{Gd2} = 7/2$ and two $S_{rad1} = S_{rad2} = 1/2$. With lowering the temperature, the $\chi_M T$ value increases more and more rapidly to reach 23.92 cm³ mol⁻¹ K at 2.0 K. Such a behavior is characteristic



Fig. 1 Molecular structure of $[{Gd(hfac)_3}_2(NITPhIm)_2]$ 1. Fluorine atoms are omitted for clarity.

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Fig. 2 $\chi_{\rm M}T$ vs. T plot for 1 (circles) and 2 (squares). The solid line represents the calculated behavior for 1 (see text).

of a system with ferromagnetic interactions. Moreover, this latter value is larger than the 20.25 cm³ mol⁻¹ K expected for a S = 9/2 (the {Gd(Nit)₂}) and a Gd ion with no interaction, thus ferromagnetic interactions also take place between these spin units along the chain. Based on above structural analysis, three main exchange pathways should be operative: (i) the magnetic interaction between Gd(1) ion and the directly coordinated nitroxide group (J₁); (ii) the magnetic coupling between the two coordinated nitroxide groups through Gd(1) (J₂); (iii) the magnetic coupling between Gd(2) and nitroxide group through phenyl and imidazole rings. The latter is anticipated to be weak.¹⁶ Hence, the magnetic behavior of **1** can be treated as that of one Rad–Gd–Rad magnetic unit plus an uncoupled Gd(III) ion, there weak exchange interaction being considered within the mean field approximation (zJ').¹⁷

The magnetic data were analyzed by a theoretical expression (see ESI[†]) deduced from the spin Hamiltonian H = $-J_1(\mathbf{S}_{\text{Rad1}}\mathbf{S}_{\text{Gd1}} + \mathbf{S}_{\text{Gd1}}\mathbf{S}_{\text{Rad2}}) - J_2\mathbf{S}_{\text{rad1}}\mathbf{S}_{\text{rad2}}$. Best fit to the experimental data yielded g = 2.0, $J_1 = 3.53 \text{ cm}^{-1}$, $J_2 = -8.93 \text{ cm}^{-1}$, $zJ' = 0.017 \text{ cm}^{-1}$. These results indicate that the Gd-Nit interactions are ferromagnetic whereas interaction between radicals through the Gd atom is antiferromagnetic, as already observed in such compounds.^{13,14} Not unexpectedly, the ferromagnetic interaction between the nitroxide and the Gd atom through phenyl and imidazole rings is quite weak due to poor spin delocalization.^{16,18} The *M* vs. *H* curve at 2.0 K is shown in Fig. S6 (ESI[†]). A magnetization of 15.90 μ_B is reached at 5 T, in agreement with 16 $\mu_{\rm B}$ expected for the ferromagnetic arrangement of the spins. For the lower fields the magnetization for 1 is above the magnetization calculated with the Brillouin function for non-coupled S = 9/2 and S = 7/2 spin centers (g = 2.0, T = 2 K); this is a further confirmation of the ferromagnetic interactions taking place between the LnRad₂ units and the bridging Ln ion. AC magnetic susceptibility measurements show that no magnetic ordering occurs above 2 K for 1 (Fig. S8).

For complex **2**, the $\chi_M T$ value at room temperature is 28.5 cm³ mol⁻¹ K, close to expected value of 29.1 cm³ mol⁻¹ K for two uncorrelated Dy(III) (a ${}^{6}\text{H}_{15/2}$ ion) and two uncorrelated S = 1/2 spins. The $\chi_M T$ value is almost constant until about 130 K where it decreases to reach 23.20 cm³ mol⁻¹ K at 2.0 K. This decrease can be ascribed to the crystal field effect for the Dy ion leading to a deviation from a Curie behavior.^{19–21}

Below 4 K a drastic modification of the curvature can be noticed, suggesting an upturn for lower *T*. The field dependence of the magnetization recorded at 2 K (Fig. S9, ESI[†]) exhibits fast increase of the magnetization for low fields followed be a steady increase to become 12 $\mu_{\rm B}$ at 50 kOe without reaching saturation.

The temperature dependence of the ac magnetic susceptibility for 2 at different frequencies ($H_{ac} = 3$ Oe) has been investigated in the absence and with an applied static field. In the absence of field, a signal for the imaginary component of the susceptibility, $\chi_{M}^{\prime\prime}$, is found for temperatures below 15 K and the signal is frequency dependent (Fig. S10, ESI⁺). However, the curve diverges from the characteristic Gaussian-shape; signal is weak and steadily increases for lower temperatures, no maximum is observed down to 2.0 K. Such a behavior suggests occurrence of relaxation mechanisms such as quantum tunneling of the magnetization.²² It can be seen from Fig. 3 (left) that the dynamic AC response is notably changed when recorded with a static field of 3 kOe. The signal for γ_{M} " deviates from zero below 16 K and well-shape peak-like curves are obtained. Both the in-phase and out-of-phase susceptibilities are strongly frequency-dependent. For χ_{M}'' , the low and high frequency signals are rather sharp but for intermediate frequencies the curves become broader. The occurrence of two distinct peaks for χ_M'' is evident for frequencies between 200 and 600 Hz. For χ_M two maxima centered at ca. 3 and 13 K are clearly visible. The Arrhenius plot obtained from these data is given in Fig. 3 (right). Obviously two relaxation regimes take place with a smooth transition between them. Analysis of the linear parts of the curve on the basis of the Arrhenius law for a thermally activated mechanism, $\tau = \tau_0 \exp(\Delta/k_{\rm B}T)$ where τ is the relaxation time and Δ the effective energy barrier for reversal of the magnetization, yielded for the low-temperature



Fig. 3 (Left) Temperature dependence of the out-of-phase ac susceptibilities measured in H = 3 kOe dc field for 2. (Right) Arrhenius plot (circles), the lines show the linear fit to the data, in blue low *T*/frequency domain, in red high *T*/frequency domain. $T_{\rm B}$ corresponds to the temperature of the maximum of $\chi_{\rm M}$ " for a given frequency.

(frequency) domain $\Delta = 17.1$ K and $\tau_0 = 17.5 \times 10^{-6}$ s, and for the high *T* (frequency) part $\Delta = 82.7$ K and $\tau_0 = 8.8 \times 10^{-8}$ s.

The AC data for compound 2 can be seen as a snapshot revealing the variety of spin-arrangements existing for this well-defined chemical system in the considered temperature domain. The signal in the low-temperature domain (2-4 K) is attributed to a SMM, typically the {DyNit₂} units, whereas signature for a SCM is found above 10 K. The hypothesis that these unusual AC features result from two independent anisotropic centers,²³ *i.e.* the {DyNit₂} unit and the bridging Dy ion, can be discarded because of the ferromagnetic interactions existing between the Ln centers as shown for 1. Moreover, the two energy barriers (Δ) obtained for 2 well compare with those reported for a discrete {DyNit}₂ complex²⁴ and a {DyNit} chain,¹² respectively. The much broader peaks observed in χ'' vs. T between these two limit situations can be attributed to spin arrangements of various correlation lengths. Analysis of the Argand plots (see ESI[†]) is revealing an α parameter close to zero (single relaxation process) for the temperature range 8-10 K whereas for temperatures below α increases in agreement with a wide distribution of τ . Considering the weak exchange coupling along the chain suggested by Gd derivative 1, the occurrence of ordered spin-chains should be very small. This is in line with the rather feeble signal for χ_M'' observed for the higher frequencies/temperatures. Conversely, for a {Dy-Nit} exchange interaction in the order of that found for Gd,^{25,26} a strong contribution from the {DyNit₂} units to χ_M'' can be expected below 4 K, thus occulting the smaller contribution from the 1-D system. This is supported by the plot of χ_{M}'' vs. Frq (Fig. 3 bottom right) that exhibits a smooth shift in frequency for the maximum as a function of T but with a significant variation of χ_M'' .

In conclusion, compound **2** appears to be a model example for size effects on the dynamic susceptibility behavior. Its dynamic susceptibility behavior encompasses contributions from a range of spin-arrangements spanning from a discrete spin cluster, *i.e.* the {DyNit₂} unit, to the 1-D ferromagnetic spin arrangement. This is probably because of a favorable ratio between the exchange interaction within the {LnNit₂} unit and that between the magnetic centers along the chain arrangement. The behavior found for 2 also suggests that the fast relaxation by quantum tunneling for the {DyNit₂} moiety is intrinsic to the unit and not related to crystal arrangement. In agreement with earlier observations,²⁴ this QT is reduced when the unit is exchange coupled with neighboring magnetic centers, allowing observation of the chain behavior even without an applied field. The role of the anisotropy of the Ln ion on this peculiar behavior is currently being examined.

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