Single-Molecule Magnets

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Dinuclear Dysprosium(III) Single-Molecule Magnets with a Large Anisotropic Barrier**

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Due to the large intrinsic magnetic anisotropy of the lanthanide ions, rare-earth metal systems, and in particular dysprosium (Dy) based materials, have sparked increasing interest in the area of molecular magnetism.[1] In a molecular complex, when such a unique property is combined with a high-spin ground state (*S*), slow relaxation of the magnetization can be obtained as seen for single-molecule magnets (SMMs).[2] Although, a number of mixed transition-metal/lanthanide SMMs have been reported,[3] pure lanthanide SMMs are relatively scarce.[1b,4] The latter molecules are rare owing to the difficulty in promoting magnetic interactions in these systems. These interactions are attained by the overlap of bridging ligand orbitals with the 4f orbitals of the lanthanide ions. Thus, ligand design is one of the key components for achieving such interactions in pure lanthanide-based systems.

To induce significant magnetic interaction between the lanthanide ions and synthesize high-energy-barrier SMMs, we have been investigating the use of (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine (H_2hmi) as a rigid chelate in lanthanide chemistry. Such a linear ligand provides O,N,O,O-based multichelating sites that are especially favorable for lanthanide ion complex formation.[5,6] They can form dinuclear systems using the bridging phenoxide oxygen atom, and the pyridine group promotes the formation of extended networks that can control the organization of the SMM units in the three-dimensional structure. Herein we report the use of the H_2hmi ligand to design materials based on ferromagnetically coupled dinuclear dysprosium(III) SMMs with large relaxation barriers.

$[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]$ (**1**) and $[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]_\infty\cdot MeCN$ (**2**·MeCN) were obtained from a suspension of $Dy(NO_3)_3\cdot 5H_2O$ / H_2hmi in methanol (treated with triethylamine) and in a 3:1 mixture of acetonitrile and methanol (treated with pyridine), respectively. After two days, pale orange single crystals were obtained, which were kept in contact with the mother liquor to prevent deterioration. Complexes **1** (Figure 1) and **2** (Figure 2) crystallize in monoclinic $P2_1/c$ and orthorhombic *Pbca* space groups, respectively. Both complexes have similar dinuclear

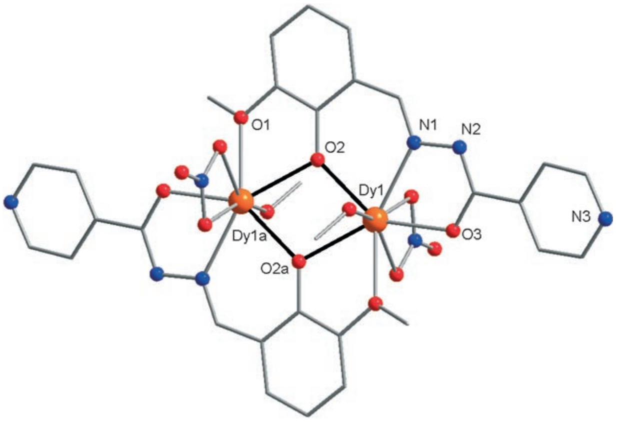

Figure 1. The molecular structure of the centrosymmetric complex $[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]$ (**1**). Symmetry-equivalent positions are denoted by an "a". Orange (Dy), Red (O), Blue (N).

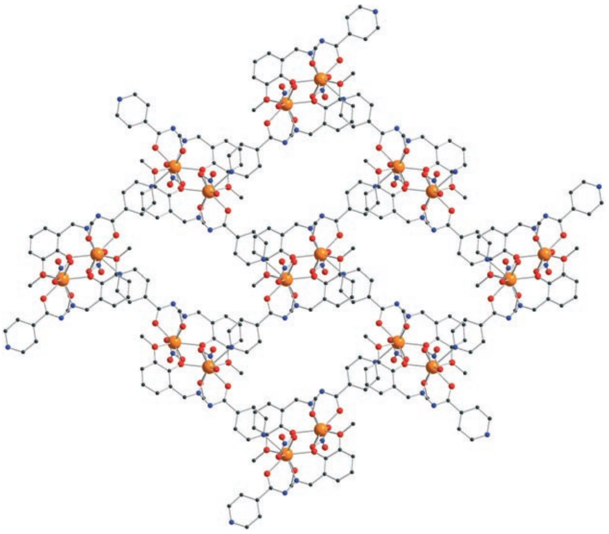

Figure 2. 2D network of complex $[Dy_2(hmi)_2(NO_3)_2(MeOH)_2]_\infty$ (**2**) as viewed along the *c* axis. Orange (Dy), Red (O), Blue (N).

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dysprosium(III) cores in which the metal centers are bridged by the phenoxide groups of two hmi ligands with Dy–O–Dy angles of 106.41° (**1**) and 107.68° (**2**). The remaining coordination sites of the lanthanide ions are filled by N and O atoms of the hmi ligands, two nitrate anions, and two methanol molecules. In the case of **2**, the pyridyl N atoms further coordinate to the dysprosium atoms of neighboring complexes forming a two-dimensional network of the dinuclear dysprosium complexes (Figure 2).

The magnetic properties of **1** and **2** are similar, as expected for compounds with closely related repeating dinuclear dysprosium units (Figure 3). At room temperature, the χT values of 30.4 and 30.0 $cm^3 K mol^{-1}$ for **1** and **2** are in good agreement with the expected value of 28.34 $cm^3 K mol^{-1}$ for two dysprosium(III) ions.[1c,7]

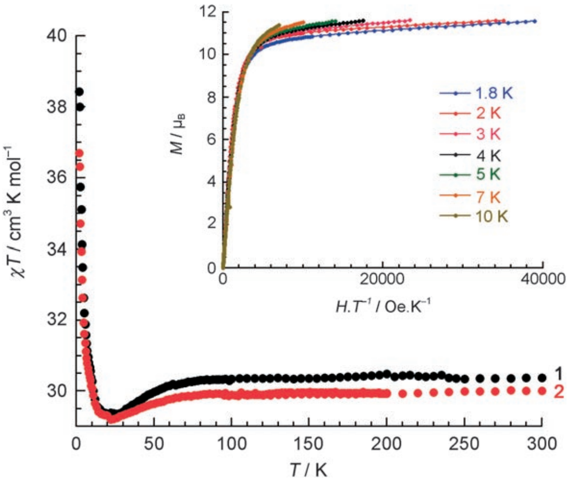

Figure 3. Temperature dependence of the χT product at 1000 Oe for **1** and **2** (with $\chi = M/H$ normalized per mol); Inset: M vs. H/T plot at low temperatures for **2**.

For both complexes, the χT product remains roughly constant before reaching a minimum value of 29.3 $cm^3 K mol^{-1}$ at 23 K. χT then increases sharply to a maximum value of 38.4 $cm^3 K mol^{-1}$ (**1**) and 36.6 $cm^3 K mol^{-1}$ (**2**) at 1.8 K. The increase of χT at low temperature suggests the presence of intramolecular ferromagnetic interactions between the metal centers. At higher temperatures, these interactions are masked by the thermal population of the excited states of the dysprosium(III) ions as is often observed in dysprosium complexes.[8]

The M vs H data below 10 K show a rapid increase in the magnetization at low magnetic fields (Supporting Information, Figures S1, S2). This is expected for materials having ferromagnetically coupled spins. At higher fields, M increases linearly up to 11.9 μ_B (**1**) and 11.6 μ_B (**2**) at 1.8 K and 7 T without clear saturation. This high-field variation and the non-superposition on a single mastercurve of the M vs H/T data (inset in Figure 3; Supporting Information, Figure S1) suggest the presence of a significant magnetic anisotropy and/or low-lying excited states in these systems. In addition, it is worth mentioning that the M vs H data do not exhibit a hysteresis effect above 1.8 K with sweep rates used in a traditional SQUID magnetometer (100–300 $Oe\,min^{-1}$). Nevertheless, below 12 K (at about 1500 Hz), an out-of-phase ac signal indicates a slow relaxation of the magnetization (Figure 4; Supporting Information, Figures S3 and S4).

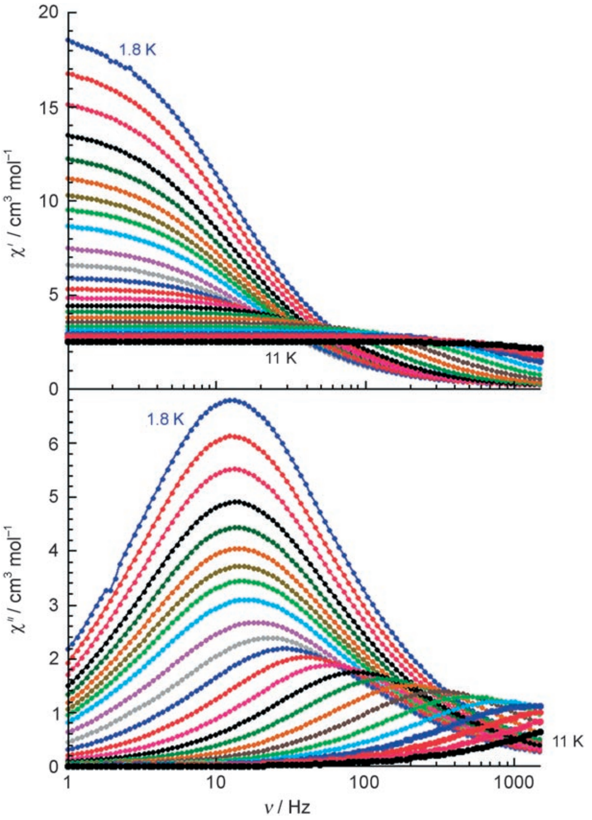

Figure 4. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility from 1.8 to 3.2 K at an interval of 0.2 K and from 3.5 to 11 K at an interval of 0.5 K under zero dc field for **2**.

The shape and frequency dependence of the ac susceptibility signal indicate the SMM nature of **1** and **2**. The magnetization relaxation time (τ) is derived from the frequency-dependence measurements and is plotted as a function of $1/T$ (between 1.8 and 10 K) in Figure 5. Below 2 K, the dynamics of **1** and **2** become temperature independent as expected[2] in a pure quantum regime with a τ value of 0.3×10^{-2} for **1** and 1.2×10^{-2} s **2**. Above 2 K, the relaxation becomes thermally activated (Arrhenius-like behavior) when thermal relaxation becomes faster than quantum relaxation. Based on the data above 8 K, remarkably large energy barriers are observed at 56 K and 71 K, and the pre exponential factors of the Arrhenius laws (τ_0) are 3×10^{-7} s for **1** and 7×10^{-8} s for **2**.

In these compounds, the absence of the M vs. H hysteresis loop above 1.8 K is caused by the presence of a relatively fast zero-field relaxation. Therefore, to minimize this effect, ac susceptibility measurements have been performed under applied dc fields (Supporting Information, Figures S5–S8). The results demonstrate that for **2,** the relaxation time is significantly increased under a dc field in the temperature range 2–6 K, in which the quantum relaxation process is

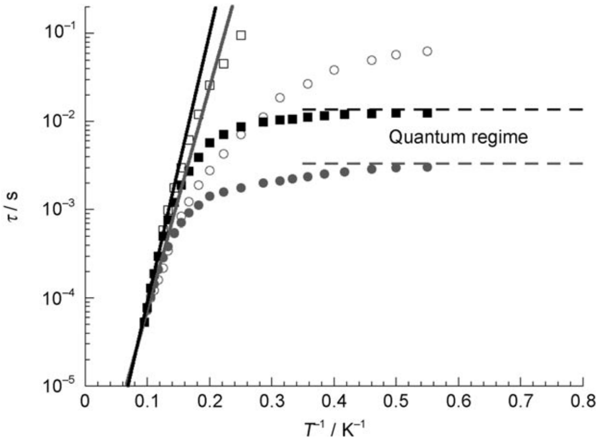

Figure 5. Magnetization relaxation time (τ) versus T^{-1} plot for **1** and **2** under zero dc field (● and ■ respectively) and under the optimum dc fields (○ and □, at 800 and 700 Oe for **1** and **2**, respectively). The solid lines correspond to the Arrhenius laws.

effective. On the other hand, τ is less or not influenced above 8 K in the thermally activated regime.

The quantum relaxation is minimized at 800 and 700 Oe for **1** and **2**, respectively, as shown by the minimum of the characteristic frequency observed at 5 K and 8 K for **2** and 5 K for **1** (Supporting Information, Figure S9). Therefore, the ac susceptibility has been measured at those optimum fields to follow the thermally activated regime at lower temperatures (Supporting Information, Figures S10, S11). Above 7 K, the obtained relaxation time for both compounds under a dc field correlates with the zero-field measurements (Figure 5), indicating a pure thermal relaxation. Figure 5 also indicates that for **2**, the relaxation time at 700 Oe is in agreement with the zero-field Arrhenius law confirming the minimization of the quantum effects by the applied dc field. However, below 5 K, the quantum processes influence significantly the relaxation even under applied field (700 Oe). For **1**, a magnetic field of 800 Oe seems to have a less influence on the quantum relaxation as τ deviates from the thermal regime at about the same temperature as in a zero dc field.

In conclusion, rare dinuclear dysprosium(III) SMMs with remarkably large energy barriers are synthesized using the rigid H_2hmi ligand. The rationally designed ligand promotes ferromagnetic interaction between the dysprosium(III) ions and further organizes the SMMs into networks using the pyridine group. Although frequency-dependent ac signals above 30 K were observed for mononuclear lanthanide complexes,[1b] no energy barrier was reported. Thus, to our knowledge, **2** has the largest energy barrier reported for a lanthanide complex. This energy barrier is also one of the highest values for a SMM.[9]

Experimental Section

1: A suspension of $Dy(NO_3)_3 \cdot 5H_2O$ (0.165 g, 0.37 mmol) and H_2hmi (0.068 g, 0.25 mmol) in MeOH (20 mL) was treated with Et_3N (0.141 mL, 1 mmol). The resulting pale yellow solution was stirred for a further 15 min, filtered, and the filtrate left undisturbed at room temperature. After two days, X-ray-quality pale orange crystals were formed, which were collected by filtration, washed with MeOH, and dried in vacuum. Yield: 35 %. The sample was maintained in contact with the mother liquor to prevent deterioration of the crystals, which have been identified crystallographically as **1**. Selected IR data for **1** (KBr): $\tilde{\nu} = 3421$(br), 1601(s), 1572(m), 1521(s), 1458(s), 1407(w), 1381(s), 1328(w), 1267(w), 1240(m), 1219(s), 1169(w), 1097(w), 1076(m), 1057(m), 1010(w), 959(m), 907(w), 845(m), 783(w), 741(s), 695(m) cm^{-1}.

2: A suspension of $Dy(NO_3)_3 \cdot 5H_2O$ (0.165 g, 0.37 mmol) and H_2hmi (0.068 g, 0.25 mmol) in MeCN/MeOH (15 mL:5 mL) was treated with pyridine (0.081 mL, 1 mmol). The resulting yellow solution was stirred for a further 15 min, filtered, and the filtrate left undisturbed at ambient temperature. After two days, X-ray-quality pale orange crystals were formed, which were collected by filtration, washed with a MeCN/MeOH mixture, and dried in vacuum. Yield: 40 %. The sample was maintained in contact with the mother liquor to prevent deterioration of the crystals, which have been identified crystallographically as the polymer **2**·MeCN. Selected IR data for **2** (KBr): $\tilde{\nu} = 3415$(br), 1610(s), 1572(m), 1522(s), 1459(s), 1383(s), 1307(m), 1263(m), 1244(m), 1221(m), 1077(m), 1013(w), 961(w), 914(w), 855(w), 789(w), 740(m), 704(m), 688(w) cm^{-1}.

Crystal structure data for **1**: $C_{30}H_{28}Dy_2N_8O_{14}$, crystal size: $0.15 \times 0.12 \times 0.10$ mm^3, monoclinic, $P2_1/c$, $a = 9.6976(10)$, $b = 10.5912(10)$, $c = 17.2186(17)$ Å, $\beta = 95.4300(10)°$, $V = 1760.6(3)$ $Å^3$, $T = 203(2)$ K, $Z = 2$, $\rho_{calcd} = 1.980$ $g\,cm^{-3}$, $\mu(\lambda = 0.71073$ Å$) = 4.291$ mm^{-1}, 17911 reflections collected, 4212 unique ($R_{int} = 0.0401$), $R1 = 0.0315$ and $wR2 = 0.0707$ using 3246 reflections with $I > 4\sigma(I)$.

Crystal structure data for **2**·MeCN: $C_{64}H_{66}Dy_4N_{18}O_{28}$, crystal size: $0.20 \times 0.15 \times 0.10$ mm^3, orthorhombic, $Pbca$, $a = 18.496(3)$, $b = 14.486(2)$, $c = 14.326(2)$ Å, $V = 3838.3(10)$ $Å^3$, $T = 203(2)$ K, $Z = 2$, $\rho_{calcd} = 1.891$ $g\,cm^{-3}$, $\mu(\lambda = 0.71073$ Å$) = 3.941$ mm^{-1}, 30478 reflections collected, 3906 unique ($R_{int} = 0.0611$), $R1 = 0.0350$ and $wR2 = 0.0832$ using 2918 reflections with $I > 4\sigma(I)$.

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[1] a) S. Bertaina, S. Gambarelli, A. Tkachuk, I. N. Kurkin, B. Malkin, A. Stepanov, B. Barbara, *Nat. Nanotechnol.* **2007**, *2*, 39; b) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694; c) C. Benelli, D. Gatteschi, *Chem. Rev.* **2002**, *102*, 2369, and references therein.

[2] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66; b) L. Thomas, L. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, *383*, 145.

[3] a) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, *J. Am. Chem. Soc.* **2004**, *126*, 420; b) A. Mishra, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 15648; c) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, *Angew. Chem.* **2004**, *116*, 4002; *Angew. Chem. Int. Ed.* **2004**, *43*, 3912; d) F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, *J. Am. Chem. Soc.* **2006**, *128*, 1440; e) M. Ferbinteanu, T. Kajiwara, K.-Y. Choi, H. Nojiri, A. Nakamoto, N. Kojima, F. Cimpoesu, Y. Fujimura, S. Takaishi, M. Yamashita, *J. Am. Chem. Soc.* **2006**, *128*, 9008; f) G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, *Chem. Commun.* **2007**, 1807; g) C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J.-F. Jacquot, D. Luneau, *Angew. Chem.* **2006**, *118*, 4775; *Angew. Chem. Int. Ed.* **2006**, *45*, 4659; h) V. Mereacre, A. M. Ako, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, A. K. Powell, *Chem. Eur. J.* **2008**, *14*, 3577; i) J.-P. Costes, S. Shova, W. Wernsdorfer, *Dalton Trans.* **2008**, 1843.

[4] a) J. Tang, I. J. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem.* **2006**, *118*, 1761; *Angew. Chem. Int. Ed.* **2006**, *45*, 1729; b) N. Ishikawa, *Polyhedron* **2007**, *26*, 2147, and references therein.
[5] M. Diop, F. B. Tamboura, M. Gaye, A. S. Sall, A. H. Barry, T. Jouini, D. Senegal, *Bull. Chem. Soc. Ethiop.* **2003**, *17*, 167.
[6] X-H. Bu, M. Du, L. Zhang, X-B. Song, R-U. Zhang, T. Clifford, *Inorg. Chim. Acta* **2000**, *308*, 143.
[7] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.
[8] M. L. Kahn, R. Ballou, P. Porcher, O. Kahn, J-P. Sutter, *Chem. Eur. J.* **2002**, *8*, 525, and references therein.
[9] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 2755.