

Influence of ligand substitution on magnetic hyperfine interaction in Dy₆-based single-molecule magnets/toroics

Lena Scherthan¹ · Thomas Ruppert² · Yan Peng² · Amer Baniodeh² · Hendrik Auerbach¹ · Tim Hochdörffer¹ · Juliusz A. Wolny¹ · Wenli Bi^{3,4} · Jiyong Zhao³ · Michael Y. Hu³ · Thomas S. Toellner³ · E. Ercan Alp³ · Dennis E. Brown⁵ · Christopher E. Anson² · Annie K. Powell^{2,6} · Volker Schünemann¹

Published online: 28 November 2019
© Springer Nature Switzerland AG 2019

Abstract

¹⁶¹Dy time-domain synchrotron Mössbauer spectroscopy (SMS), just recently presented as a novel tool to investigate Dy(III)-based single-molecule magnets (SMMs), has now been applied on two polynuclear Dy₆-based wheel compounds possessing special features of single-molecule toroics (SMTs). The magnitude of the magnetic hyperfine field revealed for the Dy₆ ring system [Dy₆(teaH)₆(NO₃)₆]·8MeOH is with $B_0 = 574.3(5)$ T characteristic for Dy(III) with a ⁶H_{15/2} ground state. The ligand substituted compound [Dy₆(Me-teaH)₆(NO₃)₆]·6MeCN possesses within the experimental errors the same magnetic hyperfine characteristics ($B_0 = 574.9(5)$ T). Consequently, the herein studied organic ligand variation has no perceptible influence on the magnetic hyperfine field sensed by the ¹⁶¹Dy(III) nuclei in these particular homometallic Dy(III)₆-wheels.

Keywords Time-domain Mössbauer spectroscopy/nuclear forward scattering · Dysprosium · Magnetic hyperfine field · Single-molecule magnets

1 Introduction

With the contemporary evolution of the research fields of spintronics, molecular electronics and quantum computing, single-molecule magnets (SMMs) arouse an immense amount of

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME2019), 1-6 September 2019, Dalian, China*
Edited by Tao Zhang, Junhu Wang and Xiaodong Wang

✉ Lena Scherthan
schertha@rhrk.uni-kl.de

✉ Volker Schünemann
schuene@physik.uni-kl.de

Extended author information available on the last page of the article

interest due to their intriguing magnetic and quantum properties combined on a nanoscale entity [1]. Molecular magnetic materials based on lanthanide ions as magnetic centers, and above all those incorporating Dy(III) ions, are among the best high-performance SMMs, characterized by high anisotropy barriers together with long relaxation times of the magnetization reversal [2, 3]. The recent development of Dy-based multicenter systems has further spawned so-called single-molecule toroids (SMTs), characterized by a toroidal arrangement of magnetic moments. Owing to the versatility for manipulation by external electric and magnetic fields or by current, new possibilities for multiferroic systems and for future applications regarding data storage technologies are feasible [4].

In order to contribute to the required understanding of molecular magnetic materials, we have just recently reported the use of synchrotron-based ^{161}Dy time-domain Mössbauer spectroscopy (SMS) [5], also known as Nuclear Forward Scattering (NFS), as a complementary technique to susceptibility measurements conventionally applied in the research field of SMMs [6].

To pursue our adopted line of inquiry, we have performed ^{161}Dy time-domain SMS experiments on two polynuclear SMMs incorporating Dy(III). The specific features of SMTs, namely a toroidal arrangement of local magnetic moments resulting in a non-magnetic ground state is present in these systems owing to predominant intramolecular dipolar interaction [4, 7].

The two investigated cyclic Dy_6 rings $[\text{Dy}_6(\text{teaH})_6(\text{NO}_3)_6]\cdot 8\text{MeOH}$ (**1**) [8] and $[\text{Dy}_6(\text{Me-teaH})_6(\text{NO}_3)_6]\cdot 6\text{MeCN}$ (**2**) [9], both based on triethanolamine (teaH₃) as ligand, are structurally almost isomorphous, except for the methyl present on each non-bridging arm of the ligand in compound **2**. Such an organic ligand substitution may have an impact on the electronic structure, as impressively revealed in a series of $\{\text{Fe(III)}_2\text{Dy(III)}_2\}$ compounds possessing different local hyperfine characteristics of the Fe(III) nuclei dependent on the substituent [10, 11]. Consequently, we aim to investigate the effect of a ligand substitution on the strength of the magnetic hyperfine field present at the Dy(III) nucleus in these two structurally related SMTs.

2 Materials and methods

The two Dy_6 wheels were synthesized following the description as given in ref. [8, 9], where the molecular structure and the magnetic properties are characterized in detail.

The ^{161}Dy time-domain SMS experiments were carried out at beamline 3ID-D at the Advanced Photon Source at Argonne National Laboratory, operating in its standard mode (top-up) yielding a bunch separation of 153 ns. By means of an appropriate monochromator setup [12], the synchrotron radiation was monochromatized to the 25.65 keV nuclear resonance transition energy in ^{161}Dy . In analogy to our previously reported ^{161}Dy SMS experiments [5], the polycrystalline samples were filled into a copper sample holder (geometrical sample thickness $d = 1.5$ mm) which in turn was mounted in an Oxford He-bath cryostat. The experiments were performed at $T = 4.2$ K. Each spectrum was recorded for one hour in forward scattering geometry with a detector system consisting of avalanche photodiodes with a time resolution of about 1 ns. Using conventional time-filtering methods that suppress the prompt electronic scattering, the data-collection window started 25 ns after the excitation pulse.

The data evaluation was carried out using the software package CONUSS, including routines to calculate the coherent nuclear scattering for the nuclear resonance in ^{161}Dy [13, 14]. The analysis model was based on a static Hamiltonian including Gaussian distributed magnetic hyperfine fields with zero quadrupole splitting, adopted in analogy to the previously reported results obtained on a mononuclear SMM [5]. The dimensionless effective thickness

was calculated by means of the following factors: density of Mössbauer nuclei n - deduced from the samples' compositions [8, 9], the geometrical thickness d , the resonant absorption cross section σ_0 and the natural abundance a of ^{161}Dy , $t_{\text{eff}} = f \cdot n \cdot a \cdot d \cdot \sigma_0$ [15]. The Lamb-Mössbauer factor f was included as free simulation parameter.

3 Results and discussion

The ^{161}Dy time-domain SMS spectra recorded at $T = 4.2$ K on both Dy_6 ring compounds are depicted Fig. 1. Both spectra show an exponential decay that is modulated by a regular beating structure with a period of about 5.0(1) ns for both compounds. These clearly resolved periodic beats are directly related to the energetic magnetic hyperfine splitting of the nuclear levels $|I, m_I\rangle$ with nuclear spins of $I_g = I_e = 5/2$ for the ground and excited state. With consideration of the above-mentioned limited time resolution, the beating results mainly from the two nuclear transitions nearest the resonance energy, namely $|5/2, \pm 1/2\rangle$ to $|5/2, \mp 1/2\rangle$ [5, 15]. The slope of the envelope of the time spectra is dependent on the nuclear decay time and of the effective thickness, including the fraction of recoilless events, the so-called Lamb-Mössbauer factor [15]. Moreover, in the case of relaxation times comparable to the Larmor precession of the nuclei, the decay rate is further influenced [15].

The theoretical reproduction of the experimental time-domain SMS spectra is achieved with consideration of only one single Dy(III) site. This assumption reflects the molecular symmetry (S_6) with its six electronically equivalent Dy(III) ions possessing all the same distorted square antiprismatic geometry (NO_7) [8, 9]. Furthermore, the underlying assumption of static magnetic fields is in agreement with the results of the magnetic characterization of **1** and **2** by alternating current (ac) susceptibility showing indications of slow relaxation of magnetization [8, 9]. The decay rate is however best reproduced with Lamb-Mössbauer factors of $f = 0.62(5)$ for **1** and $f = 0.69(5)$ for **2**. These values are slightly lower than the one of metallic Dy, determined to be $f = 0.78(1)$ by use of ^{161}Dy nuclear inelastic scattering experiments at 15 K [16].

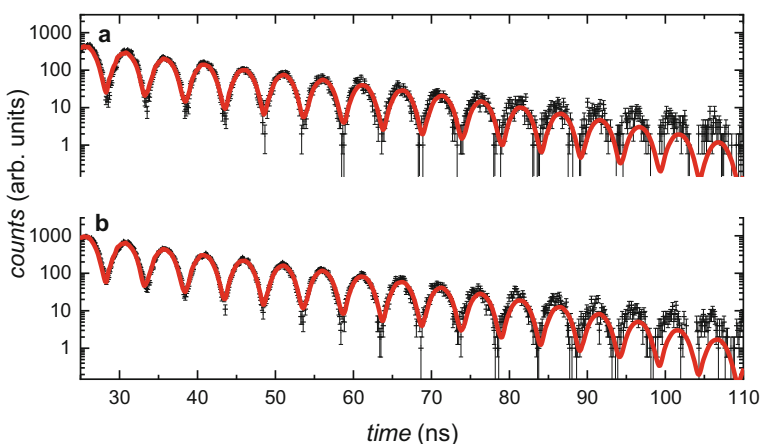


Fig. 1 ^{161}Dy time-domain SMS spectra at $T = 4.2$ K of the Dy_6 ring **1** (a) and of its ligand substituted analogue **2** (b) (black data points). The red lines display theoretical simulations obtained by use of the software CONUSS with assumption of a static Hamiltonian approach with Gaussian distributed magnetic hyperfine fields. The parameters are given in Table 1

The simulation yields magnetic hyperfine fields of $B_0 = 574.3(5)$ T with $\sigma(B_0) = 4.6(2)$ T for **1** and $B_0 = 574.9(5)$ T with $\sigma(B_0) = 4.7(2)$ T for the ligand substituted compound **2** (see Table 1). The magnitude of these observed fields is characteristic for a free Dy(III) ion with its two main contributions: firstly, the predominantly positive field stemming from the partly filled 4f electronic configuration due to the ${}^6H_{15/2}$ ground state and secondly, the negative field attributed to a core polarization, also known as Fermi-Contact term, that contributes with about 5% to the entire hyperfine field [17, 18]. The reported values for the molecular Dy₆ compounds are remarkably close to the one reported for Dy metal ($B = 574$ T, at $T = 4.2$ K [19, 20], latest results of 578.9(2) T at $T = 20$ K [21]). In metallic Dy, there exists a third contribution to the hyperfine field, namely the polarization of the conduction electrons [17, 18]. However, for the herein investigated Dy₆ compounds, an additional influence may result from the intramolecular Dy-Dy interactions, since the nearest Dy-Dy distance is only 3.73 Å [8, 9], as well as by an influence of the coordinating ligands.

In view of the further simulation parameters, it has to be noted that the magnitudes of the Gaussian distributions slightly exceed the ones obtained for the just recently investigated mononuclear SMM [5]. Furthermore, starting from 80 ns, slight deviations between the simulation and the experimental data are noticeable. These facts may be attributed to the electronic structure. There are several low-lying excited exchange states, that are only separated by an energy gap of 4.4 cm⁻¹, as revealed by theoretical ab initio calculations with consideration of exchange and dipolar magnetic interaction between the individual Dy sites [7]. Both the non-magnetic and the magnetic excited states exist, which are related by moment reversal of one single Dy ion, taking place on faster time scales than detectable with ac magnetic susceptibility (<10 μs) [7]. Regarding the ¹⁶¹Dy time-domain SMS experiments, performed at $T = 4.2$ K, corresponding to an energy of $k_B T = 2.9$ cm⁻¹, it is likely that not only the non-magnetic ground state, but also higher magnetic states are populated. Even though there is no clear indication for relaxation processes in the Mössbauer time scale (ns-range), we attribute the relatively large widths of the Gaussian distributions and the slight deviations in the simulation to the fast relaxation of magnetization related to the population of these excited states.

The comparison of the results revealed for both compounds leads to the conclusion that the substitution of methyl has no perceptible influence on the hyperfine field sensed by the ¹⁶¹Dy(III) nuclei in the herein studied Dy₆ ring systems (see Table 1). This result is in agreement with the results of the susceptibility measurements, showing that compound **2** has similar static and dynamic magnetic properties as compound **1** [9]. In fact, the hyperfine field is correlated to the static and the dynamic magnetic characteristics of SMTs. These depend on their single-ion electronic properties and the inter-ionic interactions [7], which may in turn both be steered by modifications in the ligand environment [9]. In this context, it is noteworthy that in the above mentioned series of {Fe(III)₂Dy(III)₂} compounds, the distant organic ligand

Table 1 Parameters as obtained by the analysis of the ¹⁶¹Dy time-domain SMS spectra taken at $T = 4.2$ K yielding the magnetic hyperfine field B_{eff} , the full width at half maximum σ of the Gaussian distribution as well as the Lamb-Mössbauer factors f and the effective thickness t_{eff}

Compound	B_{eff} (T)	σ (T)	f	t_{eff}
1	574.3(5)	4.6(2)	0.62(5)	50(4)
2	574.9(5)	4.7(2)	0.69(5)	52(4)

substitution did not only influence the local hyperfine fields sensed by the Fe(III) nuclei but also the static and dynamic magnetic properties. We intend to study whether this observation results from an influence of a potential cooperative magnetic coupling between the 3d and 4f metal ions.

In conclusion, we report the results of synchrotron-based ^{161}Dy time-domain SMS experiments performed on two hexanuclear molecular magnets incorporating Dy(III). Since this technique gives access to local information at the magnetic center, the local magnetic hyperfine characteristics of the Dy(III) nuclei can be explored despite the overall non-magnetic ground state of these compounds. The revealed magnetic hyperfine fields of both compounds are similar within the experimental errors, showing no obvious influence of the organic ligand substitution.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through SFB/TRR 88 3MET. The presented research used resources of the Advanced Photon Source, U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. W. B. would like to acknowledge the partial support by COMPRES, the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 1606856.

References

1. Bogani, L., Wernsdorfer, W.: *Nat. Mater.* **7**, 179 (2008)
2. Rinehart, J.D., Long, J.R.: *Chem. Sci.* **2**, 2078 (2011)
3. Liu, J.-L., Chen, Y.-C., Tong, M.-L.: *Chem. Soc. Rev.* **47**, 2431 (2018)
4. Ungur, L., Lin, S.-Y., Tang, J., Chibotaru, L.F.: *Chem. Soc. Rev.* **43**, 6894 (2014)
5. Scherthan, L., Schmidt, S.F.M., Auerbach, H., Hochdörffer, T., Wolny, J.A., Bi, W., Zhao, J., Hu, M.Y., Toellner, T., Alp, E.E., Brown, D.E., Anson, C.E., Powell, A.K., Schünemann, V.: *Angew. Chem. Int. Ed. Eng.* **58**, 3444 (2019)
6. Sieklucka, B., Pinkowicz, D.: *Molecular magnetic materials. Concepts and applications.* Wiley-VCH, Weinheim (2017)
7. Ungur, L., Langley, S.K., Hooper, T.N., Moubaraki, B., Brechin, E.K., Murray, K.S., Chibotaru, L.F.: *J. Am. Chem. Soc.* **134**, 18554 (2012)
8. Langley, S.K., Moubaraki, B., Forsyth, C.M., Gass, I.A., Murray, K.S.: *Dalton Trans.* **39**, 1705 (2010)
9. Baniodeh, A., Magnani, N., Bräse, S., Anson, C.E., Powell, A.K.: *Dalton Trans.* **44**, 6343 (2015)
10. Mereacre, V., Baniodeh, A., Anson, C.E., Powell, A.K.: *J. Am. Chem. Soc.* **133**, 15335 (2011)
11. Vieru, V., Ungur, L., Cemortan, V., Sukhanov, A., Baniodeh, A., Anson, C.E., Powell, A.K., Voronkova, V., Chibotaru, L.F.: *Chem. Eur. J.* **24**, 16652 (2018)
12. Toellner, T.S., Hu, M.Y., Bortel, G., Sturhahn, W., Shu, D.: *Nucl. Inst. Methods Phys. Res. A.* **557**, 670–675 (2006)
13. W. Sturhahn, CONUSS is free software available via <http://www.nrixs.com/conuss.html>
14. Sturhahn, W.: *Hyperfine Interact.* **125**, 149 (2000)
15. R. Röhlberger: *Nuclear Condensed Matter Physics with Synchrotron Radiation* Springer-Verlag STMP 208, Berlin Heidelberg, (2004)
16. Chumakov, A.I., Rüffer, R., Leupold, O., Barla, A., Thiess, H., Gil, J.M., Alberto, H.V., Vilao, R.C., Ayres de Campos, N., Kohn, V.G., Gerken, M., Lucht, M.: *Phys. Rev. B.* **63**, (2001)
17. Rechenberg, H.R., Bogé, M., Jeandey, C., Oddou, J.L.: *Solid State Commun.* **64**, 277 (1987)
18. Ofer, S., Rakavy, M., Segal, E., Khurgin, B.: *Phys. Rev.* **138**, (1965)
19. Nowik, I., Ofer, S., Wernick, J.H.: *Phys. Lett.* **20**, (1966)
20. Greenwood, N.N., Gibb, T.C.: *Mössbauer Spectroscopy.* Chapman and Hall Ltd., London (1971)
21. Shvyd'ko, Y.V., Gerken, M., Franz, H., Lucht, M., Gerdau, E.: *Europhys. Lett.* **56**, 309 (2001)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Affiliations

Lena Scherthan¹ · Thomas Ruppert² · Yan Peng² · Amer Baniodeh² · Hendrik Auerbach¹ · Tim Hochdörffer¹ · Juliusz A. Wolny¹ · Wenli Bi^{3,4} · Jiyong Zhao³ · Michael Y. Hu³ · Thomas S. Toellner³ · E. Ercan Alp³ · Dennis E. Brown⁵ · Christopher E. Anson² · Annie K. Powell^{2,6} · Volker Schünemann¹

¹ Department of Physics, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

² Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

³ Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

⁴ Department of Geology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

⁵ Department of Physics, Northern Illinois University, DeKalb, IL 60115, USA

⁶ Institute of Nanotechnology, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany