Hyperfine coupling and slow magnetic relaxation in isotopically enriched Dy III mononuclear single-molecule magnets

J. Flores Gonzalez, F. Pointillart, O. Cador

To cite this version:
J. Flores Gonzalez, F. Pointillart, O. Cador. Hyperfine coupling and slow magnetic relaxation in isotopically enriched Dy III mononuclear single-molecule magnets. Inorganic Chemistry Frontiers, Royal Society of Chemistry, 2019, 6 (4), pp.1081-1086. 10.1039/c8qi01209a. hal-02122161

HAL Id: hal-02122161
https://hal-univ-rennes1.archives-ouvertes.fr/hal-02122161
Submitted on 1 Apr 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Hyperfine coupling and slow magnetic relaxation in isotopically enriched Dy\textsuperscript{III} mononuclear single-molecule magnets\textsuperscript{†}

Jessica Flores Gonzalez, Fabrice Pointillart\textsuperscript{ID} and Olivier Cador\textsuperscript{ID} *

The four main stable isotopes of the \([^{161}\text{Dy}]\text{(tta)}_3(\text{L})\text{C}_6\text{H}_{14}\) \((^{4}\text{Dy} \text{ with } A = 161–164)\) Single-Molecule Magnet (SMM) \((\text{tta}^- = 2\text{-thenoyltrifluoroacetone})\) and \(\text{L} = 2\text{-(2-methylpyridyl)-4,5,4,5-bis(propphythio)-tetraethylfulvalenyl}-1\text{-H-benzimidazol-2-yl} \) have been magnetically investigated and structurally characterized by single crystal X-ray diffraction. The two nuclear spin-free \(^{162/164}\text{Dy}\) behave the same from a dynamic magnetic point of view and with slower magnetic relaxation than the two pure magnetically active isotopically substituted \(^{161/163}\text{Dy}\). In addition, this paper demonstrates that \(^{164}\text{Dy}\) and \(^{163}\text{Dy}\) relax differently even if they both carry \(I = 5/2\) nuclear spin. After the release of the dipolar interactions through magnetic dilution, \((^{161}\text{Dy}_{0.05}\text{Y}_{0.95}\text{(tta)}_3(\text{L})\text{C}_6\text{H}_{14}\) \((^{161}\text{Dy@Y})\) relaxes four times slower than \(^{163}\text{Dy@Y}\) due to different hyperfine coupling constants.

Introduction

The possibility to observe a magnetic memory at the single-ion level for a lanthanide ion was demonstrated in 2003 for a \([\text{TbPc}_2]\) \((\text{Pc} = \text{phthalocyaninato})\) complex.\textsuperscript{1,2} Since that discovery, lanthanide-based mononuclear Single-Molecule Magnets (SMMs) have been designed for their potential applications in high-density data storage\textsuperscript{3} and spintronic devices.\textsuperscript{4}

On one hand, the integration of lanthanide SMMs in devices for data storage is limited due to the low-temperature range at which such molecular systems highlight magnetic memory. To overcome such a limitation, few strategies have been explored: (i) a molecular engineering strategy to induce an adequate symmetry and crystal field around the lanthanide ion leading to an optimal crystal splitting of the ground multiplet state. Such a strategy has recently driven chemists to design a hexa-tert-butyl dysprosocenium complex with an exceptional magnetic axiality and a blocking temperature of 60 K;\textsuperscript{5,6,7,10} (ii) the minimization of the magnetic moment perturbation by magnetic dilution by adding to the complex a frozen solution\textsuperscript{11} or doping it with a diamagnetic isomorphous matrix\textsuperscript{12} which leads to the isolation of the electronic spin carriers; and (iii) the minimization of the hyperfine interactions by isotopic enrichment in nuclear spin-free lanthanides which leads to a diminution of the Quantum Tunneling of Magnetization (QTM) efficiency.\textsuperscript{13,14}

On the other hand, lanthanide SMMs could be suitable to perform nuclear spin qubits/qudits\textsuperscript{4,15–18} due to the several DiVincenzo characteristics\textsuperscript{19,20} already observed for such systems. In other words, two nuclear isomers of a lanthanide SMM could be used to enhance the magnetic performance for data storage (nuclear spin-free isomer) while the pure nuclear spin isomer could be used as a multilevel nuclear spin qubit (qudit) because of the nuclear-spin-driven QTM events.\textsuperscript{21} Nevertheless the Dy\textsuperscript{III} ion is composed of seven isotopes with nuclear spin values of 0 and 5/2. The four main \(^{161}\text{Dy}, 162\text{Dy}, 163\text{Dy}\) and \(^{164}\text{Dy}\) isotopes represent 97.5% of the isotopic mixture but until now only two of them have been studied on the same system.\textsuperscript{13,14,21}

In this paper, we propose to go a step further in studying four stable isotopically enriched dysprosium complexes \(([^{4}\text{Dy}(\text{tta})_3(\text{L})]\text{C}_6\text{H}_{14})\) \(22\) where \(\text{tta}^- = 2\text{-thenoyltrifluoroacetone}\), \(\text{L} = 2\text{-(2-methylpyridyl)-4,5,4,5-bis(propphythio)-tetraethylfulvalenyl}-1\text{-H-benzimidazol-2-yl} \) and \(A = 161, 162, 163\) and 164 (abbreviated as \(^{4}\text{Dy}\) hereafter). It is worth noting that \(^{161}\text{Dy}\) and \(^{164}\text{Dy}\) have been previously studied by some of us.\textsuperscript{13} The aim of this study was to pursue the investigations on an identical system for which all the synthetic steps are under control. The two \(^{163}\text{Dy}\) and \(^{163}\text{Dy}\) isotopes possess the same nuclear spin value \(I = 5/2\) but not the same nuclear magnetic moment while the \(^{163}\text{Dy}\) and \(^{164}\text{Dy}\) isotopes possess no nuclear spins. Magnetic dilution of the dysprosium complexes in an isomorphous diamagnetic matrix based on yttrium \((^{4}\text{Dy@Y})\) has been systematically performed to cancel dipolar interactions in the condensed phase.
Materials and methods

The elemental analyses of the compounds were performed at the Centre Régional de Mesures Physiques de l’Ouest, Rennes. The Dy/Y ratio of the compounds $^{162}\text{Dy} @ \text{Y}$ and $^{164}\text{Dy} @ \text{Y}$ was determined using SEM (Scanning Electron Microscopy). All observations and measurements were carried out with a JEOL JSM 6400 scanning electron microscope (JEOL Ltd, Tokyo, Japan) with an EDS (Energy Dispersive Spectrometry) analysis system (Oxford Link INCA). The voltage was kept at 9 kV, and the samples were mounted on carbon stubs and coated for 5 min with a gold/palladium alloy using a sputter coater (Jeol JFC 1100). This analysis has been performed by the “Centre de Microscopie Electronique à Balayage et microAnalyse (CMEBA)” from the University of Rennes 1 (France). The dc magnetic susceptibility measurements were performed on solid polycrystalline samples with a Quantum Design MPMS-XL SQUID magnetometer between 2 and 300 K in an applied magnetic field of 200 Oe for temperatures between 2 and 20 K, 2 kOe between 20 and 80 K and 10 kOe above 80 K. Making measurements at various applied fields allows us to verify that the samples are free from ferromagnetic impurities and also avoid saturation phenomena at low temperature. These measurements were all corrected for the diamagnetic contribution as calculated with Pascal’s constants.

Experimental

All solvents were dried using standard procedures. 4,5-Bis(pro-pylythio)-tetrathiafulvalene-2-(2-pyridyl)benzimidazole-methyl-2-pyridine ligand (L) was synthesized following a published procedure. The isotopically enriched Dy$_2$O$_3$ oxides are commercially available from Eurisotop company. All other reagents were purchased from Aldrich Co. Ltd and were used without further purification.

Isotopically enriched Dy(tta)$_3$$^2$H$_2$O compounds are prepared according to the following modified literature procedure: On one side, 47.1 mg (0.126 mmol) of Dy$_2$O$_3$ enriched at 94.4% in $^{162}$Dy$^{III}$ or at 95.0% in $^{163}$Dy$^{III}$ were placed in the presence of 130 μL of concentrated HCl. After 30 min of stirring at 50 °C, the resulting solution of DyCl$_3$$^6$H$_2$O was diluted with 1 mL of water. On the other side, 224 mg of Htta (1.010 mmol) were dissolved in 180 mL of water at 60 °C under intense stirring. The pH of the solution was adjusted to 6–6.5 with NH$_4$OH. To the obtained solution was added an aqueous solution of isotopically enriched DyCl$_3$$^6$H$_2$O (0.252 mmol). The pH of the solution was adjusted to 7–7.5 during the stirring and then flocculation of Dy(tta)$_3$$^2$H$_2$O took place and was filtered. Yield $^{162}$Dy(tta)$_3$$^2$H$_2$O: 115 mg (53%). Yield $^{163}$Dy(tta)$_3$$^2$H$_2$O: 110 mg (51%).

$^{162/164}$Dy(tta)$_3$$^2$H$_2$O compounds are prepared according to the following modified literature procedure: on one side, 47.1 mg (0.126 mmol) of Dy$_2$O$_3$ enriched at 94.4% in $^{162}$Dy$^{III}$ or at 95.0% in $^{163}$Dy$^{III}$ were placed in the presence of 130 μL of concentrated HCl. After 30 min of stirring at 50 °C, the resulting solution of Dy$_2$O$_3$ enriched at 94.4% in $^{162}$Dy$^{III}$ or at 95.0% in $^{163}$Dy$^{III}$ was filtered. Yield $^{162}$Dy$_2$O$_3$: 50.0 mg (85%). Yield $^{163}$Dy$_2$O$_3$: 50.0 mg (85%).

Results and discussion

Structural description

The four compounds $^{162}$Dy, $^{164}$Dy, $^{162}$Dy@$^\text{Y}$ and $^{164}$Dy@$^\text{Y}$ are isosstructural (Table S1, Fig. S1–S4‡). The ratio Dy/$^\text{Y}$ (0.05/0.95) for the two doped compounds $^{162}$Dy$_{0.05}$Y$_{0.95}$tta$_3$L$^2$H$_2$O ($^{162}$Dy@$^\text{Y}$) and $^{163}$Dy$_{0.05}$Y$_{0.95}$tta$_3$L$^2$H$_2$O ($^{163}$Dy@$^\text{Y}$) has been determined by EDS analysis and then it is used to refine the X-ray structure on single crystals. The X-ray structures for the natural isotopes, $^{162}$Dy and $^{164}$Dy, have been studied in our previous work. This single and rapid structural description is given below to understand the structural characteristic of the system.

The X-ray structures consist of a mononuclear complex of Dy$^{III}$ which lies in a N$_2$O$_6$ coordination environment with a square antiprism symmetry. Three tta– anions and the ligand L provide the six oxygen and two nitrogen atoms, respectively (Fig. 1). As expected, the Dy–N bond length is longer than the Dy–O ones due to the oxophilic character of the lanthanide. The central C=C bond length and the non-planar TTF core confirm the neutrality of L. The crystal packing highlighted the formation of “head-to-tail” dimers of complexes (Fig. S5†).

**Fig. 1** Molecular structure of $^{163}$Dy. Hydrogen atoms and CH$_2$Cl$_2$ molecule of crystallization are omitted for clarity.
Static magnetic properties

The thermal dependence of the magnetic susceptibility and the first magnetization at 2 K are measured for the $^{162}\text{Dy}$ and $^{164}\text{Dy}$ samples and for $^{162}\text{Dy}@$Y and $^{163}\text{Dy}@$Y (Fig. S6 and S7†). The $\chi_M T$ vs. $T$ and $M$ vs. $H$ curves are identical for the two isotopes because the static magnetic properties are independent of the nuclear magnetic moment. The experimental values are in agreement with the expected values for a single $\text{Dy}^{3+}$ ion.25

Dynamic magnetic properties

The dynamic magnetic properties of the two isotopologues $^{162}\text{Dy}$ ($I = 0$) and $^{163}\text{Dy}$ ($I = 5/2$) are determined by measuring the frequency dependences of the magnetic susceptibility (Fig. 2, S9 and S10†). Both isotopologues display a frequency dependence for the out-of-phase component, $\chi_M''$, of the ac susceptibility in a zero external dc field, a sign of slow magnetic relaxation. As previously observed for $^{161}\text{Dy}$ and $^{164}\text{Dy}$, the maximum on the $\chi_M''$ vs. $\nu$ curve (where $\nu$ is the frequency of the oscillating field) occurs at a lower frequency for the nuclear spin-free isotope (16 Hz) than for the isotope with $I = 5/2$ (160 Hz).

The relaxation times ($\tau$) for both isotopologues have been extracted with an extended Debye model (see the ESI†). Their temperature dependences follow a modified Arrhenius law ($\tau^{-1} = \tau_0^{-1} \exp(\Delta/|T|) + \tau_1^{-1}$) where $\tau_0$ and $\tau_1$ are, respectively, the intrinsic and temperature-independent relaxation times and $\Delta$ is the energy barrier) (Fig. 3, Tables 1, S2 and S3†). Both $\Delta$ and $\tau_0$ remain almost identical for $^{162}\text{Dy}$ and $^{163}\text{Dy}$, suggesting that the thermally activated regime is not affected by the nucleus and thus by the hyperfine interactions (Table 1, Fig. S11 and S12†), while the thermally independent regime (QTM) is strongly affected by the isotopic enrichment with the cancellation of the nuclear spin of dysprosium (Fig. 3). Even if the QTM is reduced, it is still operative at a low temperature. To cancel this, an optimal magnetic field of 1000 Oe is applied (Fig. S13–S16†), leading to a drastic slowing down of the magnetic relaxation. Nevertheless, such an intense magnetic field also cancels the isotopic effect. In fact the two Arrhenius plots for both $^{162}\text{Dy}$ and $^{163}\text{Dy}$ are superimposed (Fig. S17†). Fig. 3 provides an easy comparison between all isotopologues. As expected, the two nuclear spin-free isotopes $^{162}\text{Dy}$ and $^{164}\text{Dy}$ behave the same whereas the two isotopes $^{161}\text{Dy}$ and $^{163}\text{Dy}$ ($I = 5/2$) display faster magnetic relaxation. In the QTM regime, a significant difference exists between $^{161}\text{Dy}$ and $^{163}\text{Dy}$. Fig. 4 shows the $\chi_M''$ vs. $\nu$ curves for the two $^{161}\text{Dy}$ and $^{163}\text{Dy}$ with respective maxima centred at 106 Hz and 160 Hz, respectively. $^{161}\text{Dy}$ relaxes slightly faster than $^{163}\text{Dy}$. This can be compared with the very different (of opposite sign) hyperfine coupling constants of $^{161}\text{Dy}$ and $^{163}\text{Dy}$.26 Furthermore, the hyperfine interactions are expected to be stronger for the isotope $^{163}\text{Dy}$ than for $^{161}\text{Dy}$.27 leading to a more efficient QTM for the former as experimentally observed (Fig. 3 and Table 1). The effect of the nuclear spin value and, a fortiori, the effect of the hyperfine constant value are very sensitive to any magnetic field (external or internal) because the hyperfine interaction, of the order of a few thousandths of wavenumber, is easily destroyed by the dipolar magnetic field generated by intermolecular interactions. In order to evaluate the exact effect of the hyperfine coupling constants for the two $^{161}\text{Dy}$ and $^{163}\text{Dy}$ isotopes, the internal magnetic field has been released in the doped samples [($^{161}\text{Dy}_{0.03}\text{Y}_{0.97}$][ta][L])·C$_6$H$_{14}$ ($^{161}\text{Dy}@$Y, the data come from our previous work13] and [($^{163}\text{Dy}_{0.05}\text{Y}_{0.95}$][ta][L])·C$_6$H$_{14}$ $^{163}\text{Dy}@$Y. The frequency dependences, in the zero external field, of the two doped isotopo-

![Fig. 2](image2.png) Frequency dependences of $\chi''_M$ of $^{162}\text{Dy}$ and $^{163}\text{Dy}$ in a zero magnetic field in the temperature range of 2–15 K.

![Fig. 3](image3.png) Temperature dependences of the relaxation times $\tau$ of the four main stable isotopologues $^{161}$–$^{164}\text{Dy}$ (full circles) and diluted samples $^{161}$–$^{164}\text{Dy}@$Y in a zero magnetic field in the temperature range of 2–15 K. Full lines are guides to the eye only.
The cancelling of the internal magnetic field has two consequences on the magnetic properties of the doped samples: (1) the maxima of the out-of-phase component of the magnetic susceptibility are shifted to lower frequencies for both $^{161}$Dy@Y ($0.2\text{ Hz}$) and $^{163}$Dy@Y ($0.8\text{ Hz}$) with respect to the condensed phase (Fig. 3 and Tables 1, S7†). This is even true at the lowest temperatures where the relaxation time becomes almost 1000 times slower than that in the condensed phase. (2) The difference between the two doped isotopologues ($^{161}$Dy@Y and $^{163}$Dy@Y) is much more pronounced, with, at $2\text{ K}$, the relaxation time of $^{161}$Dy@Y being four times slower than that of $^{163}$Dy@Y. Considering that the magnetic entities in $^{161}$Dy@Y and $^{163}$Dy@Y are perfectly isolated systems, the difference observed is entirely due to hyperfine coupling. As expected, the relaxation tends to become thermally independent at low temperature. Therefore, a hyperfine coupling effect on the magnetic relaxation of a molecule can only be probed in diluted systems. Of course, the release of the hyperfine coupling in nuclear spin-free systems such as $^{162}$Dy@Y and $^{164}$Dy@Y produces slower relaxation (Fig. 3 and Table S6†) which never ends in a thermally independent regime at low temperature. At this stage, relaxation is governed by Orbach or Raman processes or a combination of these two processes.

**Fig. 4** Frequency dependences of $\chi''_M$ of $^{161}$Dy and $^{163}$Dy in a zero magnetic field in the temperature range of 2–14 K.

**Fig. 5** Frequency dependences of $\chi''_M$ of $^{161}$Dy@Y and $^{163}$Dy@Y in a zero magnetic field in the temperature range of 2–15 K.

### Table 1 Dynamic parameters of the four, pure and diluted, isotopologues of Dy

| Isotopologue | $^{161}$Dy | $^{162}$Dy | $^{163}$Dy | $^{164}$Dy |
|--------------|------------|------------|------------|------------|
| $\Delta/K$   | 43         | 45         | 44         | 46         |
| $\tau_0/s$   | $6.7(1) \times 10^{-6}$ | $6.0(8) \times 10^{-6}$ | $7.8(1) \times 10^{-6}$ | $5.6(7) \times 10^{-6}$ |
| $\sigma_\text{v}/\text{s}^b$ | $1.8(1) \times 10^{-3}$ | $1.3(1) \times 10^{-3}$ | $8.1(1) \times 10^{-3}$ | $1.0(1) \times 10^{-3}$ |
| $\Delta/K$   | Not measured | $58$ | $59$ | $57$ |
| $\tau_0/s$   | $4.0(10) \times 10^{-6}$ | $3.5(9) \times 10^{-6}$ | $3.9(6) \times 10^{-6}$ | $3.8(8) \times 10^{-6}$ |
| $\sigma_\text{v}/\text{s}^b$ | $0.83(6)$ | $\approx 100^b$ | $0.19(0.4)$ | $\approx 100^b$ |

*a* Values extracted from the experimental data at 2 K. *b* Values obtained by extrapolation of the experimental data.
**Conclusions**

The two 162 and 163 isotopes of the DyIII mononuclear Single-Molecule Magnet [Dy(tta)_3(L)]_2C_6H_4 were investigated and then compared with the two 161 and 164 isotopes previously studied by some of us. The nuclear spin-free isotope of Dy displayed a slower magnetic relaxation in the thermally independent regime compared to the isotope of Dy due to the cancelling of the hyperfine interactions coming from the metal centre. As expected, the two nuclear spin-free Dy and Dy behaved as the same while a significant difference of the relaxation time of magnetization was observed between the two Dy and Dy isotopic isomers. At 2 K, the Dy isotope relaxed 50% faster than Dy because of the greater hyperfine interaction constants for the former compared to the latter. Finally after removing the dipolar magnetic interactions by doping, the effect of the hyperfine interaction constants on magnetic relaxation is directly observed with Dy which relaxed 300% faster than Dy.

Future DyIII isotopic enrichment in which DyIII is in a nuclear spin-free environment is under investigation in order to determine the effect of the hyperfine coupling arising from the first neighbouring atoms and the effect of the oblate versus prolate electronic distribution of the lanthanide ion.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the CNRS, Université de Rennes and the European Research Council through the ERC-CoG 725184 MULTIPROSMM (project no. 725184).

**Notes and references**

1. R. Giraud, W. Wernsdorfer, A. M. Tkachuk, D. Mailly and B. Barbara, Phys. Rev. Lett., 2001, 87, 057203.
2. N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, J. Am. Chem. Soc., 2003, 125, 8694–8695.
3. D. Gatteschi, R. Sessoli and J. Villain, Molecular Nanomagnets, Oxford University Press, 2006.
4. S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben and W. Wernsdorfer, Science, 2014, 344, 1135–1138.
5. F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkanmäki and R. A. Layfield, Angew. Chem., Int. Ed., 2017, 56, 11445–11449.
6. C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, Nature, 2017, 548, 439–442.
7. F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkanmäki and R. A. Layfield, Science, 2018, eaav0652.
8. L. Ungur, S.-Y. Lin, J. Tang and L. F. Chibotaru, Chem. Soc. Rev., 2014, 43, 6894–6905.
9. Z. Zhu, M. Guo, X.-L. Li and J. Tang, Coord. Chem. Rev., 2019, 378, 350–364.
10. P. Zhang, Y.-N. Guo and J. Tang, Coord. Chem. Rev., 2013, 257, 1728–1763.
11. G. Cosquer, F. Pointillart, S. Golhen, O. Cador and L. Ouahab, Chem. – Eur. J., 2013, 19, 7895–7903.
12. F. Habib, P. H. Lin, J. Long, I. Korobkov, W. Wernsdorfer and M. Murugesu, J. Am. Chem. Soc., 2011, 133, 8830–8833.
13. F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab and O. Cador, Angew. Chem., Int. Ed., 2015, 54, 1504–1507.
14. Y. Kishi, F. Pointillart, B. Lefèvre, F. Riobé, B. Le Guennic, S. Golhen, O. Cador, O. Maury, H. Fujiwara and L. Ouahab, Chem. Commun., 2017, 53, 3575–3578.
15. S. Thiele, R. Vincent, M. Holzmann, S. Klyatskaya, M. Ruben, F. Balestro and W. Wernsdorfer, Phys. Rev. Lett., 2013, 111, 037203.
16. R. Vincent, Nature, 2012, 488, 357–360.
17. D. P. O’Leary, G. K. Brennen and S. S. Bullock, Phys. Rev. A, 2006, 74, 032334.
18. M. Leuenberger and D. Loss, Nature, 2001, 410, 789–793.
19 K. S. Pedersen, A.-M. Ariciu, S. McAdams, H. Weihe, J. Bendix, F. Tuna and S. Piligkos, *J. Am. Chem. Soc.*, 2016, **138**, 5801–5804.

20 D. Aguilà, L. A. Barrios, V. Velasco, O. Roubeau, A. Repollès, P. J. Alonso, J. Sesé, S. J. Teat, F. Luis and G. Aromí, *J. Am. Chem. Soc.*, 2014, **136**, 14215–14222.

21 E. Moreno-Pineda, M. Damjanović, O. Fuhr, W. Wernsdorfer and M. Ruben, *Angew. Chem., Int. Ed.*, 2017, **56**, 9915–9919.

22 T. T. da Cunha, J. Jung, M.-E. Boulon, G. Campo, F. Pointillart, C. L. M. Pereira, B. Le Guennic, O. Cador, K. Bernot, F. Pineider, S. Golhen and L. Ouahab, *J. Am. Chem. Soc.*, 2013, **135**, 16332–16335.

23 G. Cosquer, F. Pointillart, J. Jung, B. Le Guennic, S. Golhen, O. Cador, Y. Guyot, A. Brenier, O. Maury and L. Ouahab, *Eur. J. Inorg. Chem.*, 2014, **2014**, 69–82.

24 A. I. Voloshin, N. Shavaleev and V. P. Kazakov, *J. Lumin.*, 2000, **91**, 49–58.

25 O. Kahn, *Molecular magnetism*, VCH, 1993.

26 W. Ebenhöh, V. J. Ehlers and J. Ferch, *Z. Phys.*, 1967, **200**, 84–92.

27 W. J. Childs, *Phys. Rev. A*, 1970, **2**, 1692–1701.