

CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

A New D_{2d} -symmetry Dy^{III} Mononuclear Single-Molecule Magnet Containing Monodentate N-Heterocyclic Donor Ligand

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/Ya-Li Wang,^a Bin Gu,^a Yue Ma^{*},^a Cui Xing,^a Qing-Lun Wang,^a Li-Cun Li,^a Peng Cheng^a and Dai-Zheng Liao^a

Three new lanthanide complexes $[Ln(hfac)_3(pz)_2]$ ($Ln = Dy(1), Tb(2), Ho(3)$; hfac = hexafluoroacetylacetonate; pz = pyrazole) based on pyrazole have been prepared and characterized structurally. X-ray crystallographic analysis reveals that all three complexes are isomorphous. The crystal structures of them consist of mononuclear molecule unit in which center Ln^{III} ion is surrounded with a slightly distorted D_{2d} -dodecahedron LnO_6N_2 coordination sphere from three hfac anions and two pyrazole ligands. Both static and dynamic magnetic properties were studied for complex **1**, which is proved to be a rarely reported D_{2d} -symmetry Dy^{III} mononuclear single-molecule magnet containing the monodentate N-heterocyclic donor ligand, and the luminescence characterizations of complexes **1-3** in both visible and NIR regions are also studied.

Introduction

Lanthanides are strategic materials in current technology¹ and play a remarkable role in magnetism thanks to their large magnetic moments and large anisotropy.² They are becoming almost ubiquitous among single-molecule magnets (SMMs),³ which have a range of potential applications in high-density information storage⁴ and molecular spintronics.⁵

One of the most striking developments that accompanied the advent of lanthanide SMMs is the fact that slow relaxation of the magnetization can be observed in complexes that contain only a single lanthanide ion.^{3a, 6} In fact, some mononuclear lanthanide compound (Dy^{III} , Tb^{III} , Ho^{III}) in an axial crystal-field environment can exhibit slow relaxation of the magnetization,^{6a, 7} so the interest in mononuclear single-molecule magnets (mononuclear SMMs) have rapidly developed.⁸ There are still many unknown magneto-structural correlation in mononuclear Ln-based SMMs because the variety crystal fields mainly affect their magnetic behavior. Most of the Dy^{III} based SMMs are constructed by O-donor ligand because lanthanide ions are considered to be hard acids in the Pearson classification.⁹ While Ln-N bond lengths are longer than that of Ln-O, which will perhaps offer different crystal fields and further affect magnetic behavior greatly. While lanthanide mononuclear SMMs containing N-heterocyclic donor ligand,^{7a-c, 8f, 10} especially monodentate N-donor ligands have been rarely reported. Considering the above, by adopting pyrazole to the system of $Ln(hfac)_3 \cdot 2H_2O$ which has the strong electron-withdrawing effect of hfac, we report the syntheses, structures, luminescent and magnetic properties of three lanthanide mononuclear

compounds, $[Ln(hfac)_3(pz)_2]$ ($Ln = Dy(1), Tb(2), Ho(3)$) to explore how the modifying of the N-donor ligand affects the structure and magnetism of the Ln-based mononuclear SMM. All the three complexes have the unusual D_{2d} -symmetry, and complex **1** shows the typical features associated with the mononuclear SMM behavior.

Meanwhile, because lanthanide coordination compounds with electron-rich organic ligands usually show an enhanced luminescence behavior compared to free Ln^{III} cations via the so-called "antenna effect".¹¹ Ln^{III} ions can emit either in the UV-Vis or in the near infrared (NIR) region depending on their nature and coordination environment.^{11g} Lanthanide-based NIR luminescence is attracting considerable interest both in the fields of light emitting diodes, telecommunication, and medical applications.^{1b} So in this paper, the luminescent properties of complexes **1-3** in the visible and NIR regions are also investigated.

Experimental

Materials

All chemicals were performed at reagent grade. The hexafluoroacetylacetone and pyrazole were purchased from Alfa Chemical Company. Elemental analysis for C, H and N were obtained on a Perkin-Elmer elemental analyzer model 240. Luminescence spectra and Quantum yields were determined on solid samples with Edinburgh FLS-920P spectrophotometer. Variable-temperature magnetic susceptibilities were measured on a SQUID MPMS XL-7

magnetometer in the range of 2-300 K. And all the magnetic measurements were performed on crushed and compacted polycrystalline samples to avoid orientation of the anisotropic materials. Diamagnetic corrections were made with Pascal's constants for all of the constituent atoms.¹²

Syntheses of [Ln(hfac)₃(pz)₂] (Ln = Dy(1), Tb(2), Ho(3))

The three complexes were synthesized by the same procedure; the synthesis of complex **1** is detailed. Dy(hfac)₃·2H₂O (0.082g, 0.1 mmol) was dissolved in 20 mL boiling *n*-heptane and refluxed for two hours. Then the solution was cooled to 60 °C, and a 5 mL CH₂Cl₂ solution of pyrazole (0.0136g, 0.2 mmol) was added. The resulting mixture was stirred for 30 minutes at this temperature. Pale-yellow crystals of **1** suitable for X-ray analysis were isolated by cooling the solution to room temperature and keep the filtrate in a refrigerator at 4 °C for five days. Anal. Calcd (**1**) for C₂₁H₁₁DyF₁₈N₄O₆ (yield 0.0489 g, 53.2%): C, 27.42; H, 1.21; N, 6.09. Found: C, 27.55; H, 1.40; N, 6.14. IR (KBr cm⁻¹): 3419(s), 1653(vs), 1563(w), 1533(s), 1494(s), 1461(s), 1349(w), 1256(vs), 1219(s), 1142(vs), 1046(s), 939(s), 802(s), 772(s), 660(s), 588(s); Anal. Calcd (**2**) for C₂₁H₁₁TbF₁₈N₄O₆ (yield 0.0415 g, 45.3%): C, 27.53; H, 1.21; N, 6.11. Found: C, 27.59; H, 1.24; N, 5.98. IR (KBr cm⁻¹): 3420(m), 1653(vs), 1563(w), 1533(s), 1493(vs), 1461(s), 1349(m), 1256(vs), 1219(s), 1143(vs), 1046(m), 939(m), 802(s), 773(m), 661(s), 588(s); Anal. Calcd (**3**) for C₂₁H₁₁HoF₁₈N₄O₆ (yield 0.0371 g, 40.2%): C, 27.35; H, 1.20; N, 6.08. Found: C, 27.26; H, 1.14; N, 6.16. IR (KBr cm⁻¹): 3420(vs), 1654(vs), 1563(vs), 1533(s), 1495(s), 1461(s), 1349(s), 1256(vs), 1219(vs), 1142(vs), 1047(s), 940(m), 801(s), 766(s), 661(s), 588(s).¹³

X-ray crystallography

Determination of the unit cell and data collection for the complexes were performed with Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart 1000 diffractometer and equipped with a CCD camera. All of the structures were solved primarily by direct methods and refined with the full-matrix least squares techniques using SHELXS-97 and SHELXL-97 programs.^{14a, 14b} All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms.^{14c, 14d} Crystal data and details of structural determination refinement are summarized in Table 1 and the selected bond lengths and angles have been provided in the Electronic Supplementary Information, Tables S1-S3.

Results and discussion

Description of the crystal structure

The molecular structures of **1-3** are similar, which crystallize in the monoclinic *P*2₁/*c* space group. Therefore, only the structure of Dy^{III} complex **1** is described in detail (as shown in Fig. 1). In complex [Dy(hfac)₃(pz)₂], each hfac anion provides two donor oxygen atoms coordinating to Dy^{III} cation, and the other two

coordination sites of Dy^{III} are occupied by two N atoms from two pyrazole ligands to complete the eight coordination environment DyO₆N₂. The Dy-O distances range from 2.297 to 2.357 Å, while the two Dy-N bonds are 2.452 and 2.459 Å. The O-Dy-O bond angles range from 71.1 to 144.2°, the O-Dy-N bond angles range from 71.3 to 143.8°, and the N(1)-Dy(1)-N(3) bond angle is 144.2°. It is necessary to analyze the geometry exactly because the local anisotropy of the magnetic ion is strongly affected by the coordination geometry of the metallic center. The eight-coordinated geometry is mostly taken as the *D*_{2d}-dodecahedron (DD), *C*_{2v}-bicapped trigonal prism (TP) and *D*_{4d}-square antiprism (SAP). The semi-quantitative method of polytopal analysis is examined.¹⁵ The characteristic angles calculated for the polyhedron of Dy^{III} are 30.72, 34.43, 40.27, 25.91, 1.80, 2.38°, which are summarized in Table 2. These values are close to the angles (29.5, 29.5, 29.5, 29.5 and 0.0°) of ideal DD polyhedron, respectively, indicative of *D*_{2d}-symmetry (as shown in Fig. 1), which perhaps arises from the different Ln-N and Ln-O bond lengths due to the utilizing of N-donor ligand. The shortest Dy-Dy distance is 8.87 Å, and the packing diagram for **1** is given in the Electronic Supplementary Information, Fig. S1. There is no π - π stacking interaction in the system, weak intramolecular N-H...O and C-H...F hydrogen bonds were found in the complex with H...O distances of 2.72 and 2.79 Å and H...F distances in the range of 2.67-2.71 Å. The relevant dihedral angles and the *D*_{2d}-symmetry polyhedron for complexes **2** and **3** are also shown in the Electronic Supplementary Information, Table. S4 and Fig. S2.

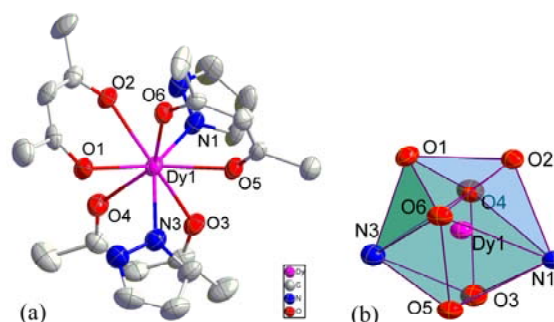


Fig. 1 (a) The molecular structure of complex **1** with thermal ellipsoids at 30% probability. Hydrogen and fluorine atoms are omitted for clarity. (b) *D*_{2d}-symmetry polyhedron of the dysprosium atom.

Luminescent properties

The luminescence properties of the rare earth complexes were investigated. The emission spectra of the samples were measured at room temperature in the solid state under excitation at 356 nm. As shown in Fig. 2a, emission peaks at 486 and 573 nm are assigned to the transitions of ⁴F_{9/2}→⁶H_{15/2} and ⁴F_{9/2}→⁶H_{13/2}, respectively, which exhibits the characteristic emissions of Dy^{III} ion.^{1b, 8c} For Tb^{III} ion, emission peaks at 489, 547, 584 and 617 nm are assigned to the ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄ and ⁵D₄→⁷F₃ transitions, respectively (Fig. 2b).^{11c} The solid-state fluorescence lifetimes of Dy (**1**) and Tb (**2**) are also studied at 298 K, giving 4.28 μs (70%) and 10.47 μs (30%)

for Dy (**1**) and a much larger 0.16 ms for Tb (**2**). For Tb (**2**) complex, the fluorescence lifetime is a little lower than 0.53 ms for [Tb(hfac)₃(H₂O)₂],^{11d} showing that the ancillary ligand of pyrazole has a detrimental effect on the luminescence of the Tb^{III} complex.

Upon excitation with UV light, we have observed characteristic emission in the NIR for the Dy^{III} ion, the emission spectrum consists of several bands at 956, 1143, 1325 and 1438 nm, which are attributed to the ⁴F_{9/2}→⁶H_{5/2}, ⁴F_{9/2}→⁶F_{3/2}, ⁶F_{1/2}+⁶H_{9/2}→⁶H_{15/2} and ⁴F_{9/2}→⁶F_{1/2} f-f transitions, respectively.^{11h}

Table 1 Crystal Data and Structure Refinements for Complexes **1-3**.

	1	2	3
Empirical formula	C ₂₁ H ₁₁ DyF ₁₈ N ₄ O ₆	C ₂₁ H ₁₁ TbF ₁₈ N ₄ O ₆	C ₂₁ H ₁₁ HoF ₁₈ N ₄ O ₆
Formula weight	919.84	916.27	922.27
Temperature / K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.8700(18)	8.9400(18)	8.9350(18)
<i>b</i> [Å]	22.049(4)	22.222(4)	22.252(4)
<i>c</i> [Å]	15.806(3)	15.950(3)	16.011(3)
α [deg]	90	90	90
β [deg]	98.02(3)	97.63(3)	97.77(3)
γ [deg]	90	90	90
Volume [Å ³]	3061.0(10)	3140.7(10)	3154.1(10)
<i>Z</i>	4	4	4
ρ_{calc} [g cm ⁻³]	1.996	1.938	1.942
μ [mm ⁻¹]	2.594	2.401	2.657
<i>F</i> (000)	1764	1760	1768
Reflections collected	17181	19188	18974
Unique / parameters	5115 / 572	5530 / 535	5549 / 535
<i>R</i> (int)	0.0531	0.0479	0.0565
Max. / min. transmission	0.695 / 0.614	0.681 / 0.625	0.654 / 0.594
Goodness-of-fit on <i>F</i> ²	1.098	1.106	1.106
<i>R</i> ₁ , <i>wR</i> ₂	0.0585, 0.1102	0.0551, 0.1340	0.0601, 0.1381
[<i>I</i> >2 σ (<i>I</i>)]			
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0859, 0.1196	0.0696, 0.1431	0.0826, 0.1497

Table 2 δ (°) and φ (°) values for Complex **1**.

	1	DD	TP	SAP
δ_1	O1-[O6-N3]-O5 ^a	30.72	29.5	0.0
δ_2	O2-[O4-N1]-O3 ^a	34.43	29.5	21.8
δ_3	O1-[O4-N3]-O3 ^a	40.27	29.5	48.2
δ_4	O2-[O6-N1]-O5 ^a	25.91	29.5	48.2
φ_1	N3-N1-O1-O2 ^b	1.80	0.0	14.1
φ_2	O6-O4-O5-O3 ^b	2.38	0.0	14.1

^a A[BC]D is the dihedral angle between the ABC plane and the BCD plane. ^b A-B-C-D is the dihedral angle between the (AB)CD plane and the AB(CD) plane, where (AB) is the center of A and B.

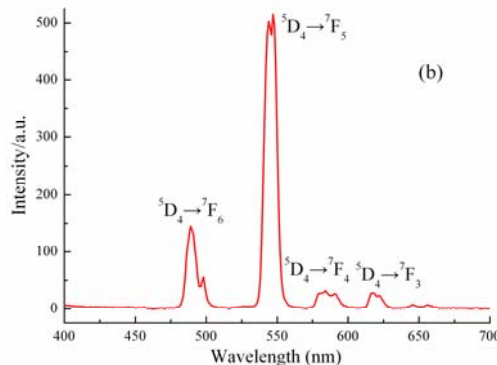
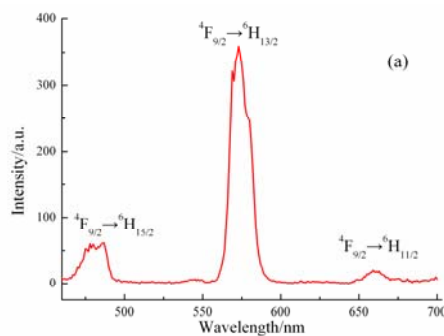


Fig. 2 The luminescence spectra of **1** (a) and **2** (b) in the solid-state at room temperature.

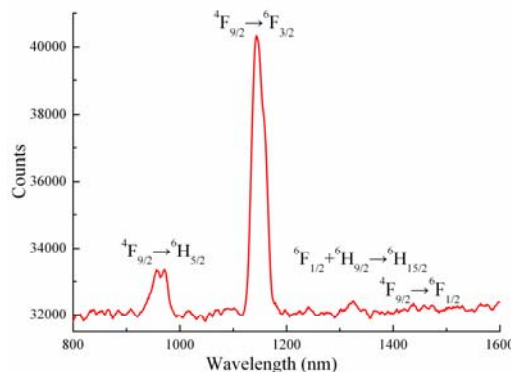


Fig. 3 NIR emission spectra of the Dy (**1**) complex in the solid-state.

Magnetic Properties

Static Magnetic Properties for **1**

Direct-current (dc) magnetic susceptibility studies of **1** were measured in an external magnetic field of 1 kOe in the range 2–300 K. At 300 K, the $\chi_M T$ value of 13.90 cm³ K mol⁻¹ is slightly lower than the theoretical values of 14.17 cm³ K mol⁻¹ for one uncoupled Dy^{III} ion ($S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$). As shown in Fig. 4, on cooling, the $\chi_M T$ value decreases gradually and reach a minimum of 12.39 cm³ K mol⁻¹ at 2 K, which may be ascribed to the thermal depopulation of the Ln^{III} Stark sublevels and/or the weak magnetic exchange between paramagnetic species in the system.

The field dependences of magnetization for complex **1** have been determined at 2 K and 6 K (inset Fig. 4). The

magnetization $6.29 \mu_B$ does not reach the theoretical value ($g_J \times J = 4/3 \times 15/2 = 10 \mu_B$), indicating the presence of magnetic anisotropy and/or low-lying excited states in the system.^{8i, 16}

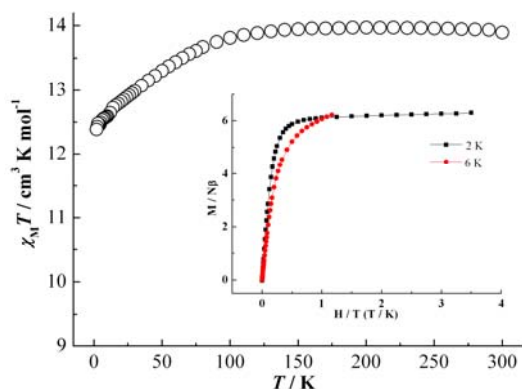


Fig. 4 Temperature dependence of $\chi_M T$ in the range of 2-300 K in 1000 Oe for **1**. Inset: M vs. H/T plot measured at different temperatures.

Dynamic Magnetic Properties for **1**

The temperature and frequency dependencies of the alternating-current (ac) susceptibilities under a zero static field were carried out (Fig. 5). From temperature dependencies of the ac susceptibility (Fig. 5, left), both the in-phase (χ') and out-of-phase (χ'') signals show a maximum. Upon cooling, χ' and χ'' start to increase again below 4 K, which is typical of quantum tunneling regime in Dy^{III} based SMMs.^{7b, 17}

From frequency dependencies of the ac susceptibility (Fig. 5, right), the magnetization relaxation time (τ) have been estimated between 2 to 10 K (Fig. 6). Analysis of the frequency dependence of the χ'' peaks through Arrhenius law [$\tau = \tau_0 \exp(U_{eff}/k_B T)$] permits the estimation of magnetization relaxation parameters: the energy barrier of 28.32 K and the pre-exponential factor (τ_0) of 4.70×10^{-6} s, which is consistent with those reported similar SMMs (in $10^{-6} \sim 10^{-11}$ s range).^{8f, 8g, 8i} Although such ac signals were observed, no hysteresis was detected in the M vs. H data at 1.9 K (Fig. S3) using a traditional SQUID magnetometer.⁸ⁱ Analyzing the slow dynamics of magnetization, Cole-Cole diagrams (Fig. 7) in the form of χ'' vs. χ' with nearly semi-circle shape have been obtained. These data have been fitted by a Debye model,¹⁸ giving the small distribution coefficient α value 0.203–0.009 (between 2-10 K), indicating the narrow distribution of relaxation times at these temperatures.

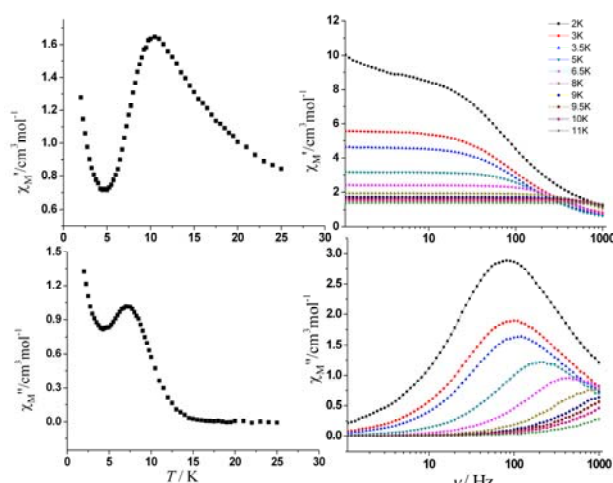


Fig. 5 Temperature (left) and frequency (right) dependence of the ac susceptibility for complex **1** as a function of the temperature below 25 K (left) and the ac frequency between 1 and 997 Hz (right) under zero static field.

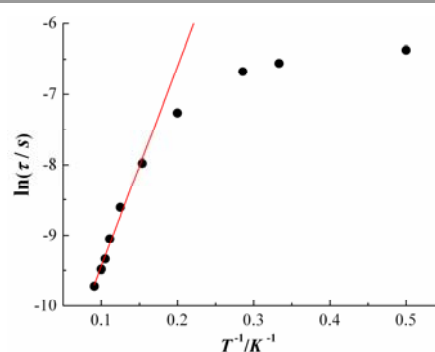


Fig. 6 Magnetization relaxation time, $\ln \tau$ vs. T^{-1} plot for **1** under zero-dc field. The solid line is fitted with the Arrhenius law.

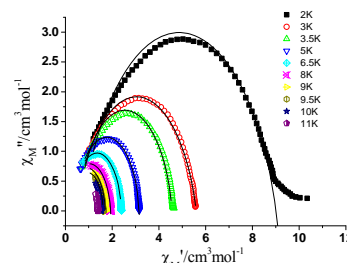


Fig. 7 Cole-Cole plots measured at 2-10 K in zero-dc field; the solid lines are the best fit to the experimental data.

All these above magnetic analysis evidences the mononuclear SMM behavior for complex **1**, which has no obvious difference in contrast to other O-donor ligands-based Dy^{III} mononuclear SMMs. The most common polyhedron for lanthanide mononuclear SMMs is D_{4d} -square antiprism geometry.^{7e, 8f, 8g, 10a} In these mononuclear SMMs, the magnetic anisotropy required for observing slow relaxation of the magnetization arises from the interaction between a single lanthanide ion and its ligand field (LF) which creates a strong preferential orientation of the magnetic moment.^{8a} Except for our complex **1**, only two compounds displays the approximate D_{2d} symmetry

around the Dy atom,^{6f, 19} at this point, more efforts are needed to be done to understand the difference.

Static Magnetic Properties for **2** and **3**

Variable-temperature magnetic susceptibilities of **2** and **3** are measured from 300 to 2 K in an applied field of 1 kOe. The χ_M and $\chi_M T$ vs. T plots are shown in Fig. 8. At 300 K, the $\chi_M T$ values are 11.87 and 14.09 cm³ K mol⁻¹, respectively, close to the expected values of 11.81 and 14.06 cm³ K mol⁻¹ for one Ln^{III} ion (⁷F₆, $g = 3/2$ for Tb^{III} and ⁵I₈, $g = 5/4$ for Ho^{III}). Upon cooling, the $\chi_M T$ values of **2** and **3** gradually decrease to reach a minimum of 6.74 and 4.33 cm³ K mol⁻¹ at 2 K, respectively. To obtain a rough quantitative estimation of the magnetic interaction between paramagnetic species, the Ln^{III} ion could be assumed to exhibit a splitting of the m_j energy levels ($\hat{H} = \Delta \hat{J}_z^2$) in an axial crystal field.²⁰ Thus the magnetic data of **2** and **3** can be analyzed by the approximate treatment, which is given in Electronic Supplementary Information of Eqs (1)-(3). In these expressions, Δ is the zero-field splitting parameter, zJ' is the intermolecular magnetic coupling parameter.²¹

The parameters obtained by the simulation of the experimental data using the above expression are $g = 1.515$, $\Delta = -0.005$ cm⁻¹, $zJ' = -0.123$ cm⁻¹ for Tb^{III} complex **2**, and for Ho^{III} complex **3**, they are $g = 1.260$, $\Delta = -0.005$ cm⁻¹, $zJ' = -0.067$ cm⁻¹. The small zJ' values are indicative of the very weak magnetic interaction between Ln^{III} ions in **2** and **3**.

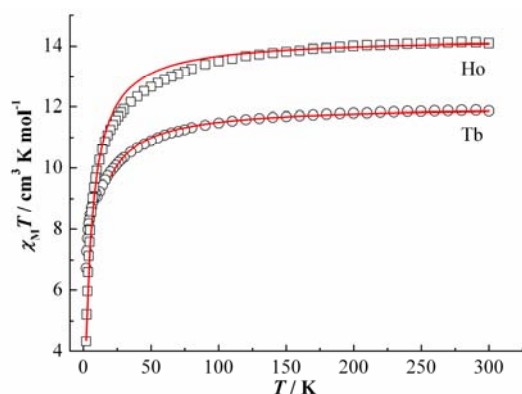


Fig. 8 Temperature dependence of $\chi_M T$ for Tb(**2**) (○) and Ho(**3**) (□) at 1000 Oe. The solid lines represent the theoretical values based on the corresponding equations.

Alternating-current susceptibilities for complexes **2** and **3** are also carried out, which are given in Electronic Supplementary Information, Fig. S4-S5. We do not observe the signal of imaginary component χ_M'' of the two complexes even at 2 K. Thus, we do not think **2** and **3** express SMMs behavior even at low temperature. This may be due to the small energy barrier which could not prevent the inversion of the spin.²²

Conclusions

We used the monodentate nitrogen heterocyclic ligand pyrazole as the ancillary ligand of Ln(hfac)₃(H₂O)₂ and reported a mononuclear single-molecule magnet containing a Dy^{III} ion

with D_{2d} -dodecahedron local symmetry. This Dy-based mononuclear SMM has an energy barrier of 28.32 K, and Dy^{III} and Tb^{III} complexes have the typical luminescence peaks. What is more, the first Dy^{III}-based mononuclear SMM containing the monodentate N-heterocyclic donor ligand with D_{2d} -dodecahedron local symmetry constitutes a new addition to the family of lanthanide based mononuclear SMM. Though the magnetic behavior of complex **1** has no obvious difference in contrast to other O-donor ligands-based Dy^{III} mononuclear SMMs, the utilizing of N-donor ligand decreases the symmetry of similar O-donor system and gives a new example of rarely reported mononuclear SMM with D_{2d} -symmetry. While how the N-donor ligand affects the magnetism is unclear up to now, further studies with other mononuclear SMMs based on N-donor ligand need to be carried out.

Acknowledgements

This work was supported by the National Natural Science Foundation of China 21101096, 90922032, 21371104, 91122013, Research Fund for the Doctoral Program of Higher Education 20100031120013, 20120031130001, Tianjin Natural Science Foundation 11JCYBJC03500.

Notes and references

^a Department of Chemistry and Key Laboratory of Advanced Energy Materials Chemistry (MOE) and TKL of Metal and Molecule Based Material Chemistry, Nankai University, Tianjin 300071, China. E-mail: maynk@nankai.edu.cn; Tel: (+86) 22-23505063.

† CCDC 803916, 806987, and 803917 contain the supplementary crystallographic data for complexes **1-3**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) available: X-ray crystallographic data for complexes **1-3** in CIF format. Selected bond lengths and angles, figures of crystal structures, luminescence measurement, and magnetic measurements. See DOI: 10.1039/b000000x/

- (a) R. Stone, *Science*, 2009, **325**, 1336-1337; (b) J. C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048-1077; (c) R. L. Carlin, *Magnetochemistry*; Springer, Berlin, 1986.
- (a) J. C. G. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897-1928; (b) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University, New York, 2006; (c) L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092-3104.
- (a) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110-5148; (b) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328-2341; (c) Y. N. Guo, G. F. Xu, P. Gamez, L. Zhao, S. Y. Lin, R. Deng, J. Tang and H. J. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 8538-8539; (d) Y. N. Guo, G. F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J. Tang, H. J. Zhang, L. F. Chibotaru and A. K. Powell, *J. Am. Chem. Soc.*, 2011, **133**, 11948-11951; (e) S. Y. Lin, W. Wernsdorfer, L. Ungur, A. K. Powell, Y. N. Guo, J. Tang, L. Zhao, L. F. Chibotaru and H. J. Zhang, *Angew.*

- Chem., Int. Ed.*, 2012, **51**, 12767-12771; (f) P. Zhang, Y. N. Guo and J. Tang, *Coord. Chem. Rev.*, 2013, **257**, 1728-1763.
- 4 (a) R. Sessoli, D. Gatteschi and J. Villain, *Molecular Nanomagnets*, Oxford University Press, New York, 2006; (b) M. Cavallini, J. Gomez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C. Rovira, J. Veciana and F. Biscarini, *Angew. Chem., Int. Ed.*, 2005, **44**, 888-892; (c) A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.*, 2007, **98**, 057201.
- 5 (a) A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer and S. Sanvito, *Nat. Mater.*, 2005, **4**, 335-339; (b) S. D. Jiang, B. W. Wang, H. L. Sun, Z. M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2011, **133**, 4730-4733; (c) L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179-186.
- 6 (a) J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078-2085; (b) G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P. Car, A. Caneschi, G. Calvez, K. Bernot and R. Sessoli, *Angew. Chem., Int. Ed.*, 2012, **51**, 1606-1610; (c) S. Takamatsu, T. Ishikawa, S. Y. Koshihara and N. Ishikawa, *Inorg. Chem.*, 2007, **46**, 7250-7252; (d) N. Ishikawa, Y. Mizuno, S. Takamatsu, T. Ishikawa and S. Y. Koshihara, *Inorg. Chem.*, 2008, **47**, 10217-10219; (e) J. L. Liu, K. Yuan, J. D. Leng, L. Ungur, W. Wernsdorfer, F. S. Guo, L. F. Chibotaru and M. L. Tong, *Inorg. Chem.*, 2012, **51**, 8538-8544; (f) M. Menelaou, F. Ouharrour, L. Rodriguez, O. Roubeau, S. J. Teat and N. Aliaga-Alcalde, *Chem. Eur. J.*, 2012, **18**, 11545-11549; (g) X. L. Li, C. L. Chen, Y. L. Gao, C. M. Liu, X. L. Feng, Y. H. Gui and S. M. Fang, *Chem. Eur. J.*, 2012, **18**, 14632-14637.
- 7 (a) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694-8695; (b) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. phys. Chem. B*, 2004, **108**, 11265-11271; (c) N. Ishikawa, Y. Mizuno, S. Takamatsu, T. Ishikawa and S. Y. Koshihara, *Inorg. Chem.*, 2008, **47**, 10217-10219; (d) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo and A. Gita-Ariño, *J. Am. Chem. Soc.*, 2008, **130**, 8874-8875; (e) M. A. Aldamen, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Arino, C. Marti-Gastaldo, F. Luis and O. Montero, *Inorg. Chem.*, 2009, **48**, 3467-3479.
- 8 (a) J. D. Rinehart and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 12558-12559; (b) J. D. Rinehart, K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7572-7573; (c) J. Ruiz, A. J. Mota, A. Rodriguez-Dieguez, S. Titos, J. M. Herrera, E. Ruiz, E. Cremades, J. P. Costes and E. Colacio, *Chem. Commun.*, 2012, **48**, 7916-7918; (d) S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Arino, A. Camon, M. Evangelisti, F. Luis, M. J. Martinez-Perez and J. Sese, *J. Am. Chem. Soc.*, 2012, **134**, 14982-14990; (e) A. Yamashita, A. Watanabe, S. Akine, T. Nabeshima, M. Nakano, T. Yamamura and T. Kajiwara, *Angew. Chem. Int. Ed.*, 2011, **50**, 4016-4019; (f) G. J. Chen, C. Y. Gao, J. L. Tian, J. Tang, W. Gu, X. Liu, S. P. Yan, D. Z. Liao and P. Cheng, *Dalton Trans.*, 2011, **40**, 5579-5583; (g) S. D. Jiang, B. W. Wang, G. Su, Z. M. Wang and S. Gao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7448-7451; (h) S. D. Jiang, S. S. Liu, L. N. Zhou, B. W. Wang, Z. M. Wang and S. Gao, *Inorg. Chem.*, 2012, **51**, 3079-3087; (i) K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. Sangregorio, M. Shanmugam, A. Caneschi, R. Sessoli and D. Gatteschi, *J. Am. Chem. Soc.*, 2009, **131**, 5573-5579; (j) N. Ishikawa, M. Sugita and W. Wernsdorfer, *J. Am. Chem. Soc.*, 2005, **127**, 3650-3651; (k) F. Branzoli, P. Carretta, M. Filibian, G. Zoppellaro, M. J. Graf, J. R. Galan-Mascaros, O. Fuhr, S. Brink and M. Ruben, *J. Am. Chem. Soc.*, 2009, **131**, 4387-4396; (l) M. Jeletic, P. H. Lin, J. J. L. Roy, I. Korobkov, S. I. Gorelsky and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 19286-19289.
- 9 (a) R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533-3539; (b) M. D. Ogden, C. L. Hoch, S. I. Sinkov, G. P. Meier, G. J. Lumetta and K. L. Nash, *J. Solution Chem.*, 2011, **40**, 1874-1888; (c) Y. Ma, G. F. Xu, X. Yang, L. C. Li, J. Tang, S. P. Yan, P. Cheng and D. Z. Liao, *Chem. Commun.*, 2010, **46**, 8264-8266.
- 10 (a) Y. Bi, Y. N. Guo, L. Zhao, Y. Guo, S. Y. Lin, S. D. Jiang, J. Tang, B. W. Wang and S. Gao, *Chem. Eur. J.*, 2011, **17**, 12476-12481; (b) Y. L. Wang, Y. Ma, X. Yang, J. Tang, P. Cheng, Q. L. Wang, L. C. Li and D. Z. Liao, *Inorg. Chem.*, 2013, **52**, 7380-7386.
- 11 (a) J.-C. G. Bünzli, *Chem. Rev.*, 2010, **110**, 2729-2755; (b) L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini and E. Tondello, *Coord. Chem. Rev.*, 2010, **254**, 487-505; (c) S. Swavey and R. Swavey, *Coord. Chem. Rev.*, 2009, **253**, 2627-2638; (d) S. V. Eliseeva, D. N. Pleshkov, K. A. Lyssenko, L. S. Lepnev, J. C. G. Bunzli and N. P. Kuzmina, *Inorg. Chem.*, 2011, **50**, 5137-5144; (e) A. Zaim, N. D. Favera, L. Guenee, H. Nozary, T. N. Y. Hoang, S. V. Eliseeva, S. Petoud and C. Piguat, *Chem. Sci.*, 2013, **4**, 1125-1136; (f) S. V. Eliseeva and J. C. G. Bunzli, *Chem. Soc. Rev.*, 2010, **39**, 189-227; (g) L. D. Carlos, R. A. S. Ferreira, V. de Zea Bermudez and S. J. L. Ribeiro, *Adv. Mater.*, 2009, **21**, 509-534; (h) P. Wang, R. Q. Fan, X. R. Liu, L. Y. Wang, Y. L. Yang, W. W. Cao, B. Yang, W. Hasi, Q. Su and Y. Mu, *CrystEngComm.*, 2013, **15**, 1931-1949.
- 12 (a) E. A. Boudreaux and L. N. Mulay, Eds. *Theory and Applications of Molecular Paramagnetism*; Wiley-Interscience, New York, 1976; (b) G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532-536.
- 13 Z. Ahmed, W. Ahmed Dar and K. Iftikhar, *Inorg. Chim. Acta.*, 2012, **392**, 446-453.
- 14 (a) G. M. Sheldrick, *SHELXS 97, Program for the solution of crystal structures*; University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL 97, Program for the refinement of crystal structures*; University of Göttingen, Germany, 1997; (c) T. Shiga, M. Ohba and H. Okawa, *Inorg. Chem. Commun.*, 2003, **6**, 15-18; (d) S. Akine, T. Matsumoto, T. Taniguchi and T. Nabeshima, *Inorg. Chem.*, 2005, **44**, 3270-3274.
- 15 (a) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748-1756; (b) T. Tsukuda, T. Suzuki and S. Kaizaki, *Inorg. Chim. Acta.*, 2005, **358**, 1253-1257; (c) M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179-275.
- 16 (a) P. H. Lin, T. J. Burchell, R. Clérac and M. M. Murugesu, *Angew. Chem., Int. Ed.*, 2008, **47**, 8848-8851; (b) S. Kanegawa, M. Maeyama, M. Nakano and N. Koga, *J. Am. Chem. Soc.*, 2008, **130**, 3079-3094.
- 17 Y. N. Guo, X. H. Chen, S. F. Xue and J. Tang, *Inorg. Chem.*, 2011, **50**, 9705-9713.
- 18 (a) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341-351; (b) S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L. C. Brunel, A. L. Rheingold, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 1999, **38**, 5329-5340.
- 19 D. P. Li, X. P. Zhang, T. W. Wang, B. B. Ma, C. H. Li, Y. Z. Li and X. Z. You, *Chem. Commun.*, 2011, **47**, 6867-6869.

- 20 (a) I. A. Kahwa, J. Selbin, C. J. O'Connor, J. W. Foise and G. L. McPherson, *Inorg. Chim. Acta.*, 1988, **148**, 265-272; (b) J. X. Xu, Y. Ma, D. Z. Liao, G. F. Xu, J. Tang, C. Wang, N. Zhou, S. P. Yan, P. Cheng and L. C. Li. *Inorg. Chem.*, 2009, **48**, 8890-8896; (c) Y. L. Wang, N. Zhou, Y. Ma, Z. X. Qin, Q. L. Wang, L. C. Li, P. Cheng and D. Z. Liao, *CrystEngComm.*, 2012, **14**, 235-239; (d) Y. Ouyang, W. Zhang, N. Xu, G. F. Xu, D. Z. Liao, K. Yoshimura, S. P. Yan and P. Cheng, *Inorg. Chem.*, 2007, **46**, 8454-8456; (e) Y. L. Wang, Y. Y. Gao, Y. Ma, Q. L. Wang, L. C. Li and D. Z. Liao, *CrystEngComm.*, 2012, **14**, 4706-4712.
- 21 Y. Liao, W. W. Shum and J. S. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 9336-9337.
- 22 T. Kajiwara, M. Nakano, K. Takahashi, S. Takaishi and M. Yamashita, *Chem. Eur. J.*, 2011, **17**, 196-205.

A New D_{2d} -symmetry Dy^{III} Mononuclear Single-Molecule Magnet Containing Monodentate N-Heterocyclic Donor Ligand

Ya-Li Wang, Bin Gu, Yue Ma*, Cui Xing, Qing-Lun Wang, Li-Cun Li, Peng Cheng, and Dai-Zheng Liao

By adopting pyrazole to the system of $Ln(hfac)_3 \cdot 2H_2O$ with the strong electron-withdrawing effect, a rarely reported D_{2d} -symmetry Dy^{III} mononuclear single-molecule magnet containing monodentate N-heterocyclic ligand was designed and synthesized successfully.

