



Canaj, A. B., Tzimopoulos, D., Kalofolias, D. A., Siczek, M., Lis, T., Murrie, M. and Milios, C. J. (2018) Heterometallic lanthanide-centred [NiIII6LnIII] rings. *Dalton Transactions*, 47(37), pp. 12863-12867. (doi:[10.1039/C8DT02855A](https://doi.org/10.1039/C8DT02855A))

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/167595/>

Deposited on: 24 August 2018

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk>

Dalton Transactions

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: A. Canaj, D. Tzimopoulos, D. A. Kalofolias, M. Siczek, T. Lis, M. Murrie and C. J. Milios, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT02855A.



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 [author guidelines](#).

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, outlined in our [author and reviewer resource centre](#), 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.



Journal Name

COMMUNICATION

Heterometallic lanthanide-centred $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}]$ rings

Angelos B. Canaj,^a Demetrios I. Tzimopoulos,^b Dimitris A. Kalofolias,^a Milosz Siczek,^c Tadeusz Lis,^c Mark Murrie^{d,*} and Constantinos J. Milios^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}]$ heptanuclear complex featuring a rare six-membered $\{\text{Ni}^{\text{II}}_6\}$ metal ring surrounding the central Dy(III) ion is reported. Magnetic studies reveal single-molecule magnet behaviour for the complex under zero external dc field, while replacing the Dy^{III} ion with Y^{III} or Gd^{III} ions allows for a comprehensive understanding of the magnetic behaviour.

Since the prototype $[\text{Mn}_{12}]$ single molecule magnet (SMM) was reported in the early 1990s,¹ the synthesis and magnetic study of 3d, 3d-4f and 4f complexes has become one of the most active areas in the field of coordination chemistry, with scientific groups worldwide trying to understand and improve the interesting magnetic properties displayed by such species.² While this task has been more than challenging, very recently species with extremely high energy barriers for the re-orientation of the magnetization, *i.e.* over 1000 K, and blocking temperatures as high as 60 K have been reported.³

Cyclic metal complexes, often reported as “metallocrowns” or “metallocoronates”, have been studied mainly for their selective ion-binding properties, but also for their intrinsic magnetic behaviour.⁴ Several examples have been reported with 3d, 3d-4f and 4f-ions, but only a handful of centred cyclic complexes have been reported.⁵ Most of the documented molecules contain Mn/Ln, Fe/Ln and Cu/Ln ions,⁶ while $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes with a centred cyclic topology are surprisingly uncommon; a CSD search revealed only three examples,⁷ none of which adopts the $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}]$ formula.

Herein, we report the first examples of centred cyclic $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}]$ (Ln = Dy, **1**; Gd, **2**; Y, **3**) complexes, with the $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}]$ analogue

showing slow relaxation of magnetisation. Solvothermal reaction of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, triethanolamine (H_3tea), NEt_3 , and the 11H-indeno[1,2-b]quinoxalin-11-one ligand, HL (Fig. S1),⁸ in MeCN for 12 h, followed by slow cooling to room temperature, led to the formation of brown plate-like crystals of $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}(\text{L})_4(\text{Htea})_4](\text{ClO}_4)_{2.5}(\text{NO}_3)_{0.5} \cdot 5.5\text{MeCN} \cdot \text{H}_2\text{O}$ ($1 \cdot 5.5\text{MeCN} \cdot \text{H}_2\text{O}$) in ~20% yield, while upon using $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the starting lanthanide salts, we were able to isolate the analogous $[\text{Ni}^{\text{II}}_6\text{Gd}^{\text{III}}(\text{L})_4(\text{Htea})_2(\text{tea})_2](\text{ClO}_4) \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ ($2 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$) and $[\text{Ni}^{\text{II}}_6\text{Y}^{\text{III}}(\text{L})_4(\text{Htea})_2(\text{tea})_2](\text{ClO}_4)_{0.5}(\text{NO}_3)_{0.5} \cdot 2.5\text{H}_2\text{O} \cdot 1.4\text{MeCN}$ ($3 \cdot 2.5\text{H}_2\text{O} \cdot 1.4\text{MeCN}$) complexes (Fig. 1, Fig. S2). All three complexes display the same $[\text{Ni}^{\text{II}}_6\text{Ln}^{\text{III}}]$ metallic core, so we will only discuss the structure of **1**.

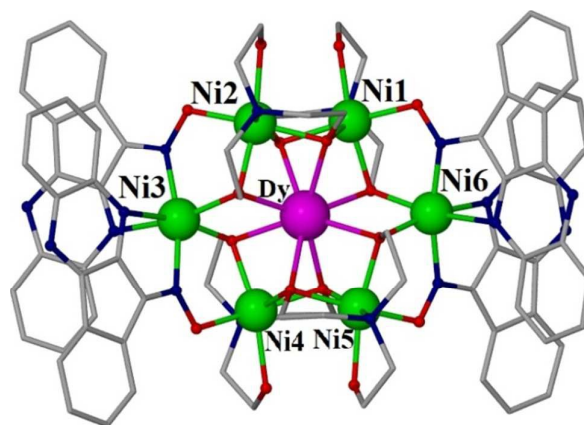


Figure 1. Molecular structure of **1**. Solvent molecules, H atoms and counterions are omitted for clarity. Colour code: Ni = green, Dy = purple, O = red, N = blue, and C = grey.

Compound **1** crystallises in the monoclinic $P2_1/n$ space group; the metallic skeleton contains six peripheral Ni^{II} ions forming a non-planar ring encapsulating the Dy^{III} ion located at its cavity. The central Dy^{III} ion is connected to the Ni^{II} ions *via* eight $\mu_3\text{-O}_R$ alkoxide groups belonging to four doubly deprotonated, Htea^{2-} ligands, which further bridge pairs of $\text{Ni}(\text{II})$ ions (Ni1-Ni2 , Ni2-Ni3 , Ni3-Ni4 , Ni4-Ni5 , Ni5-Ni6) forming the $[\text{Ni}^{\text{II}}_6\text{Dy}^{\text{III}}(\mu_3\text{-O}_R)_8]^{7+}$

^a Department of Chemistry, The University of Crete, Voutes 71003, Herakleion, Greece. E-mail: kamil@uoc.gr

^b Department of Chemistry, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece.

^c Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, Wrocław 50-383, Poland.

^d WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, UK. E-mail: Mark.Murrie@glasgow.ac.uk

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

COMMUNICATION

centred ring (Fig. S3). The Ni^{II} pairs (Ni2-Ni3, Ni3-Ni4, Ni1-Ni6 and Ni5-Ni6) are further bridged by four $\eta^1: \eta^1: \eta^1: \mu$ deprotonated L⁻ ligands through the (-N-O)_{oximate} group. The Ni-O_R-Dy angles fall into two categories: i) those between Ni3-Dy and Ni6-Dy that are 106.2-106.4° and 105.6-106.3° respectively, and ii) those between Ni1-Dy, Ni2-Dy, Ni4-Dy, Ni5-Dy that are in the narrow 84.3 - 86.4° range. Regarding the Ni-O_R-Ni angles, those between Ni1-Ni2 and Ni4-Ni5 are ~96° and ~97°, respectively, while those between Ni2-Ni3, Ni3-Ni4, Ni5-Ni6 and Ni1-Ni6 are in the 112.3-112.9° range. Finally, the Ni-N-O-Ni torsion angles fall in the 27.1-31.4° range.

All Ni^{II} ions are six-coordinate in distorted octahedral geometries, while the encapsulated Dy^{III} ion is eight-coordinate adopting distorted square antiprismatic geometry (SHAPE⁹ CShM parameter 1.025, Fig. S4, Table S2). In the square antiprismatic configuration, the distance between the two squares is defined as d_{pp} , whereas the shortest distance between ligands within one square as d_{in} ; furthermore, the angle between the diagonals of the two squares is defined as Φ , while α is the angle between the S_8 axis and a Ln-ligand direction, usually used to describe the elongation or compression along the tetragonal axes.¹⁰ For complex **1**, d_{pp} ranges from 2.496 to 2.640 Å, d_{in} is in the 2.866-3.042 Å range, Φ in the 62.4-68.3° and α varies from 60.7 to 62.1°, yielding a slightly compressed square antiprismatic environment. It has been proven by experimental and theoretical observations that for the Dy^{III} Kramers ion being in an ideal square antiprismatic geometry ($\Phi=45^\circ$, $\alpha=54.7^\circ$) with D_{4d} symmetry is an effective way to enhance the slower relaxation.¹¹

The magnetic properties of all three [Ni^{II}₆Ln^{III}] complexes were investigated by dc susceptibility measurements in the 300-2 K temperature range under a 0.1 Tesla applied magnetic field (Fig. 2). The room temperature χ_{MT} values of all complexes are close to the expected value for six non-interacting Ni^{II} ions and one Ln^{III} ion (Dy **1**, Gd **2**); the room temperature χ_{MT} value of 20.93 cm³ K mol⁻¹ for **1** is close to the theoretical value of 20.98 cm³ K mol⁻¹ expected for six non-interacting Ni^{II} ions ($g \approx 2.13$) and one Dy^{III} ion ($g \approx 1.33$). Upon cooling, χ_{MT} decreases gradually to reach a minimum value of 6.67 cm³ K mol⁻¹ at 5 K. For **2**, the room temperature χ_{MT} value of 14.62 cm³ K mol⁻¹, very close to the theoretical value of 14.68 cm³ K mol⁻¹, steadily decreases to a minimum value of 3.11 cm³ K mol⁻¹ at 5 K, while, for **3** the χ_{MT} product decreases upon cooling to reach the minimum value of 3.45 cm³ K mol⁻¹ at ~50 K, before it slightly increases to the value of 3.88 cm³ K mol⁻¹ at ~6 K. Finally, below 6 K a drop of the χ_{MT} value is observed. The χ_{MT} profile indicates the presence of either both antiferromagnetic and ferromagnetic or competing interactions within **3** (*vide infra*).

We were able to simultaneously fit the magnetic susceptibility (Fig. 2) and magnetization data (Fig. S6) for complex **3**, [Ni^{II}₆Y^{III}], adopting a 2- J model (Fig. S5, left), assuming the following two exchange interactions: i) J_1 , between Ni1-Ni6, Ni5-Ni6, Ni2-Ni3 and Ni3-Ni4 mediated by one μ_3 -O_R alkoxide (Ni-O_R-Ni $\approx 114^\circ$) and one (-N-O)_{oximate} bridge, and ii) J_2 , between Ni1-Ni2 and Ni4-Ni5 mediated through two μ_3 -O_R

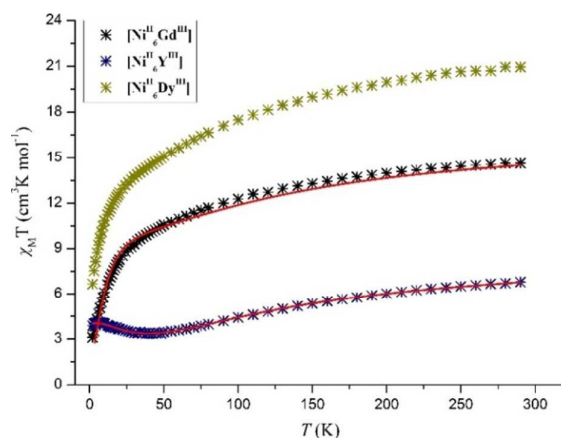


Figure 2. χ_{MT} vs T plot for complexes **1-3** under an applied dc field of 0.1 T. The solid lines represent a fit of the data in the 5–300 K range (see the text for details).

alkoxide groups (Ni-O_R-Ni $\approx 95^\circ$). Using PHI¹² and employing the Hamiltonian eqn 1:

$$\hat{H} = -2J_1 (\hat{S}_1 \hat{S}_6 + \hat{S}_5 \hat{S}_6 + \hat{S}_2 \hat{S}_3 + \hat{S}_3 \hat{S}_4) - 2J_2 (\hat{S}_1 \hat{S}_2 + \hat{S}_4 \hat{S}_5) + g\mu_B \vec{B} \sum_{i=1}^6 \vec{S}_i \quad (1)$$

gave $J_1 = -26$ cm⁻¹, $J_2 = 4$ cm⁻¹ and $g_{Ni} = 2.2$. These parameters led to an $S = 2$ ground state with the first excited state of $S = 1$ located ~18 cm⁻¹ above. The magnitude and nature of the exchange constants J_1 and J_2 are in agreement with previously reported interactions in Ni(II) complexes with similar geometric parameters; J_1 should be antiferromagnetic and the value of -26 cm⁻¹ is reasonable for Ni-O_R-Ni angles of ~114° and Ni-N-O-Ni torsion angles of ~28°, while J_2 is in excellent agreement for Ni-O_R-Ni angles below ~98°. In order to avoid over-parameterization, parameters such as zero-field splitting (ZFS) were not included in the fitting process of the magnetic susceptibility and magnetization data for complex **3**. However, including zero-field splitting (ZFS) does not significantly improve the fit.

Furthermore, we were also able to fit the magnetic susceptibility data for complex **2**, [Ni^{II}₆Gd^{III}] adopting a 3- J model (Figure S5, right) and the Hamiltonian in eqn (2):

$$\hat{H} = -2J_1 (\hat{S}_1 \hat{S}_6 + \hat{S}_5 \hat{S}_6 + \hat{S}_2 \hat{S}_3 + \hat{S}_3 \hat{S}_4) - 2J_2 (\hat{S}_1 \hat{S}_2 + \hat{S}_4 \hat{S}_5) - 2J_3 (\hat{S}_1 \hat{S}_{Gd} + \hat{S}_2 \hat{S}_{Gd} + \hat{S}_3 \hat{S}_{Gd} + \hat{S}_4 \hat{S}_{Gd} + \hat{S}_5 \hat{S}_{Gd} + \hat{S}_6 \hat{S}_{Gd}) + g_{Ni} \mu_B \vec{B} \sum_{i=1}^6 \vec{S}_i + g_{Gd} \mu_B \vec{B} \vec{S}_{Gd} \quad (2)$$

where J_1 and J_2 exchange parameters have the same meaning as in complex **3**, and J_3 describes the exchange interaction between Ni-Gd pairs. Keeping J_1 and J_2 "locked" to the values found from fitting the magnetic susceptibility of **3** (-26 and 4 cm⁻¹, for J_1 and J_2 , respectively), PHI yielded $J_3 = -0.7$ cm⁻¹, with $g_{Ni} = 2.2$ and $g_{Gd} = 2.0$. These parameters lead to an $S = 3/2$ ground-state for **2**, with the 5/2 and 7/2 excited states located at ~3 cm⁻¹ and ~8 cm⁻¹ respectively. The weak and AF character of J_3 is in good agreement with previously reported cases.¹⁴ At this point, it is worth mentioning that the majority

of {Ni^{II}-Gd^{III}} interactions is found to be ferromagnetic.¹⁵ However, according to theoretical studies performed on Ni^{II}/Gd^{III} complexes, the nature of the {Ni^{II}-Gd^{III}} interactions is strongly affected by the Ni^{II}-O-Gd^{III} angles, with smaller angles favoring antiferromagnetic interactions.¹⁶ In complex **2** the majority of the Ni^{II}-O-Gd^{III} angles is ~ 86° rationalizing the fact that J_3 is antiferromagnetic. In order to get some insight in the magnetic interaction between the Ni^{II} and Dy^{III} in **1**, we found that complex [Ni^{II}₃Dy^{III}{(py)₂C(H)O₆}(ClO₄)₃][(py)₂C(H)O⁻] is the anion of di-2-pyridylmethanol displays similar magnetic behavior where the slow relaxation observed at zero external field, albeit with a small energy barrier, is attributed to the antiferromagnetic Ni^{II}···Dy^{III} and Ni^{II}···Ni exchange interactions which help to suppress the QTM to a certain extent. However, due to the complexity of the magnetic exchange interaction between Ni^{II}···Dy^{III} within **1** it is difficult to calculate actual coupling parameters.^{16,17}

Furthermore, magnetization data were collected for all complexes (Fig. S6-S8) in the ranges of 1-5 T and 2.0-6.0 K. However, we were not able to fit the magnetization data of complex **2** (Fig. S7) assuming that only the ground state is populated.

To further investigate the magnetization dynamics of complexes **1-3**, ac susceptibility measurements were performed under a zero applied dc field. From all three complexes investigated only complex **1**, [Ni^{II}₆Dy^{III}], is likely to behave as a SMM. Complex **1** does show slow magnetic relaxation, evidenced by the fact that both the in-phase (χ_M') and out of phase (χ_M'') components show frequency and temperature dependence, with fully formed out-of-phase peaks seen for the higher frequencies, suggesting that quantum tunnelling of magnetization (QTM) takes place shortening the relaxation time (Fig. 3, Fig. S9-S10).²

An Argand plot of χ_M'' vs χ_M' is shown for **1** between 2-10 K (Fig. S11). The plots display arc like profiles and indicate one single relaxation process. The relaxation times, τ , were extracted from the fit of the Argand plot using the generalized Debye model.¹⁸ The α parameters obtained are in the range of 0.035-0.38 (2-7 K) indicating small distribution of relaxation times.¹⁹

Following the Arrhenius analysis by using the extracted relaxation times, τ , yielded a rather low effective energy barrier of $U_{eff} \approx 10$ K with $\tau_0 = 1.5 \times 10^{-5}$ s (Fig. S12) for **1**. The relatively large τ_0 value indicates the presence of QTM.²⁰ Bearing in mind that no out-of-phase signals were detected for the [Ni^{II}₆Y^{III}] analogue, we can safely assume that for the slow magnetic relaxation of **1**, the presence of the Dy^{III} ion is crucial. Importantly, the magnetic behaviour of **1** is rare since most Ni^{II}/Dy^{III} complexes reported so far do not show SMM behaviour under zero external dc field (Table S3).

In the absence of high symmetry, the ground-state of a Dy^{III} ion is a doublet along the anisotropy axis with $m_J = \pm 15/2$; thus, we were able to calculate the orientation of the anisotropy axis for the Dy^{III} ion using an electrostatic model recently reported by Chilton *et al.*, which is based on electrostatic energy minimization for the prediction of the ground state magnetic anisotropy axis.²¹ Using MAGELLAN the ground state magnetic

anisotropy axis is indicated to be tilted towards the closest negatively charged oxygen atoms of the H₃tea ligands, O2F and O2G, (Fig. S13). This method has been proven to be successful and efficient, however, the obtained results should be considered with caution due to the limitations of the electrostatic model used (*i.e.* the assumption that the negative charges sit on the atom) and the distorted square antiprismatic Dy geometry in **1**.²²

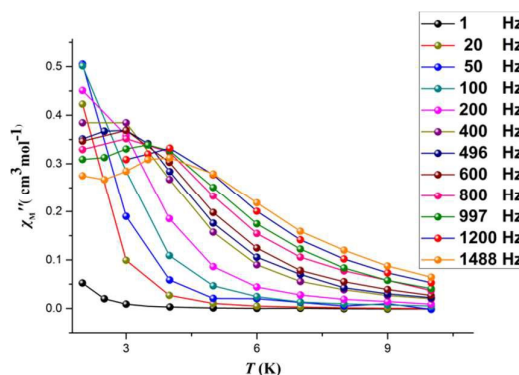


Figure 3. Plot of χ_M'' vs T for complex **1** at zero external dc field.

Conclusions

In conclusion, we have reported the first examples of heptanuclear [Ni^{II}₆Ln^{III}] (Ln = Dy, Gd, Y) complexes featuring a rare centred ring-like topology. The study of the magnetic properties revealed slow magnetic relaxation for the Dy(III) analogue under zero external dc field. Attempts to synthesize and characterize different 3d-3d' and 3d-4f cyclic centred complexes are in progress.

Conflicts of interest

The authors declare no conflicts of interest.

Notes and references

‡ CCDC reference numbers: 1849654 (for **1**), 1849655 (for **2**) and 1849653 (for **3**).

- (a) A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel and M. Guillot, *J. Am. Chem. Soc.*, 1991, **113**, 5873; (b) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; (c) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1996, **118**, 7746.
- For reviews on SMMs, see the following: (a) C. J. Milios and R. E. P. Winpenny, *Struct. Bonding* (Berlin) 2015, **164**, 1; (b) X.-Y. Wang, C. Avendaño and K. R. Dunbar, *Chem. Soc. Rev.* 2011, **40**, 3213; (c) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.* 2013, **113**, 5110; (d) S. Demir, I.-R. Jeon, J. R. Long and T. D. Harris, *Coord. Chem. Rev.* 2015, **289**, 149; (e) S.-D. Han, J.-P. Zhao, S.-J. Liu and X.-H. Bu, *Coord. Chem. Rev.* 2015, **289**, 32; (f) G. A. Craig and M. Murrie, *Chem. Soc. Rev.* 2015, **44**, 2135; (g) R. A. Layfield, *Organometallics* 2014, **33**, 1084; (h) J.-L. Liu, Y.-C. Chen and

- M.-L. Tong, *Chem. Soc. Rev.*, 2018, **47**, 2431; (i) Z. Zhu, M. Guo, X.-L. Li, J. Tang, <https://doi.org/10.1016/j.ccr.2017.10.030>; (g) A. K. Bar, P. Kalita, M. K. Singh, G. Rajaraman and V. Chandrasekhar, *Coord. Chem. Rev.*, 2018, **367**, 163; (k) S. K. Gupta and R. Murugavel, *Chem. Commun.*, 2018, **54**, 3685.
- 3 (a) Y.-S. Ding, N. F. Chilton, R. E. P. Winpenny and Y. -Z. Zheng, *Angew. Chem. Int. Ed.* 2016, **55**, 16071; (b) F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamaeki and R. A. Layfield, *Angew. Chem. Int. Ed.* 2017, **56**, 11445; (c) D. S. Krylov, F. Liu, S. M. Avdoshenko, L. Spree, B. Weise, A. Waske, A. U. B. Wolter, B. Buechner and A. A. Popov, *Chem. Commun.* 2017, **53**, 7901; (d) Y.-C. Chen, J.-L. Liu, L. Ungur, J. Liu, Q.-W. Li, L.-F. Wang, Z.-P. Ni, L. F. Chibotaru, X.-M. Chen and M.-L. Tong, *J. Am. Chem. Soc.*, 2016, **138**, 2829; (e) S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, *Chem. Sci.*, 2016, **7**, 5181; (f) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439; (g) Y.-S. Meng, L. Xu, J. Xiong, Q. Yuan, T. Liu, B.-W. Wang and S. Gao, *Angew. Chem. Int. Ed.* 2018, **57**, 1; (h) A. B. Canaj, M. K. Singh, C. Wilson, G. Rajaraman and M. Murrie, *Chem. Commun.*, 2018, **54**, 8273.
- 4 (a) G. Mezei, C. M. Zaleski and V. L. Pecoraro, *Chem. Rev.*, 2007, **107**, 4933; (b) R. W. Saalfrank and A. Scheurer, *Top. Curr. Chem.*, 2012, **319**, 125; (c) K. L. Taft, C. D. Delfs, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823; (d) A. Caneschi, A. Cornia, A. Fabretti and D. Gatteschi, *Angew. Chem. Int. Ed.* 1999, **38**, 1295; (e) J. Ummethum, J. Nehr Korn, S. Mukherjee, N. B. Ivanov, S. Stuibler, T. Strassle, P. L. W. Tregenna-Piggott, H. Mutka, G. Christou, O. Waldmann and J. Schnack, *Phys. Rev. B*, 2012, **86**, 104403; (f) M. L. Baker, T. Guidi, S. Carretta, H. Mutka, G. Timco, E. J. L. McInnes, G. Amoretti, R. E. P. Winpenny and P. Santini, *Nat. Phys.*, 2012, **8**, 906; (g) G. A. Timco, E. J. L. McInnes and R. E. P. Winpenny, *Chem. Soc. Rev.*, 2013, **42**, 1796.
- 5 (a) L. G. Westin, M. Kriticicos and A. Caneschi, *Chem. Commun.*, 2003, 1012; (b) T. Kajiwara, H. Wu, T. Ito, N. Iki and S. Miyano, *Angew. Chem., Int. Ed.*, 2004, **43**, 1832; (c) S. K. Langley, B. Moubaraki, C. M. Forsyth, I. A. Gass and K. S. Murray, *Dalton Trans.*, 2010, **39**, 1705; (d) X. Li, Y. Hung and R. Cao, *CrystEngComm*, 2012, **14**, 6045; (e) J. B. Peng, Q. C. Zhang, X. J. Kong, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 10649; (f) J.-D. Leng, J.-L. Liu and M.-L. Tong, *Chem. Commun.*, 2012, **48**, 5286; (g) S. Schmidt, D. Prodius, G. Novitchi, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun.*, 2012, **48**, 9825; (h) L.-F. Zou, L. Zhao, Y.-N. Guo, G.-M. Yu, Y. Guo, J. Tang and Y.-H. Li, *Chem. Commun.*, 2011, **47**, 8659; (i) M. Li, Y. Lan, A. M. Ako, W. Wernsdorfer, C. E. Anson, G. Buth, A. K. Powell, Z. Wang and S. Gao, *Inorg. Chem.*, 2010, **49**, 11587; (j) J. W. Sharples, Y.-Z. Zheng, F. Tuna, E. J. L. McInnes and D. Collison, *Chem. Commun.*, 2011, **47**, 7650; (k) K. H. Zangana, E. M. Pineda, E. J. L. McInnes, Jurgen Schnack and R. E. P. Winpenny, *Chem. Commun.*, 2014, **50**, 1438; (l) M. J. H. Ojeda, G. Lorusso, G. A. Craig, C. Wilson, M. Evangelisti and M. Murrie, *Chem. Commun.*, 2017, **53**, 4799; (m) K. R. Vignesh, S. K. Langley, B. Moubaraki, K. S. Murray and G. Rajaraman, *Chem. Eur. J.* 2015, **21**, 16364-16369
- 6 (a) T. T. Boron, J. C. Lutter, C. I. Daly, C. Y. Chow, A. H. Davis, A. Nimthong-Roldán, M. Zeller, J. W. Kampf, C. M. Zaleski and V. L. Pecoraro, *Inorg. Chem.*, 2016, **55**, 10597; (b) A. Deb, T. T. Boron, M. Itou, Y. Sakurai, T. Mallah, V. L. Pecoraro and J. E. Penner-Hahn, *J. Am. Chem. Soc.*, 2014, **136**, 4889-4892; (c) T. T. Boron, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 2010, **49**, 9104-9106; (d) J. Wu, L. Zhao, L. Zhang, X.-L. Li, M. Guo and J. Tang, *Inorg. Chem.*, 2016, **55**, 5514; (e) C.-S. Lim, J. Jankolovits, P. Zhao, J.W.Kampf and V. L. Pecoraro, *Inorg. Chem.*, 2011, **50**, 4832; (f) A. Baniodeh, Y. Liang, C.E.Anson, N.Magnani, A.K.Powell, A.Unterreiner, S.Seyfferle, M.Slota, M.Dressel, L.Bogani, K.Go, *Adv.Funct.Mater.*, 2014, **24**, 6280; (g) L.Rigamonti, A.Nava, M.-E.Boulon, J.Luzon, R.Sessoli, A.Cornia, *Chem.-Eur.J.*, 2015, **21**, 12171.
- 7 (a) J. Jankolovits, J. W. Kampf, V. L. Pecoraro, *Polyhedron*, 2013, **52**, 491; (b) C. G. Efthymiou, T. C. Stamatatos, C. Papatriantafyllopoulou, A. J. Tasiopoulos, W. Wernsdorfer, S. P. Perlepes, G. Christou, *Inorg.Chem.*, 2010, **49**, 9737; (c) H.L.C.Feltham, S.Dhers, M.Rouzieres, R.Clerac, A.K.Powell, S.Brooker, *Inorg.Chem.Front.*, 2015, **2**, 982.
- 8 (a) B. D. Pearson, R. A. Mitsch and N. H. Cromwell, *J. Org. Chem.*, 1962, **27**, 1674; (b) A. B. Canaj, L. E. Nodaraki, A. Philippidis, D. I. Tzimopoulos, E. Fotopoulou, M. Siczek, T. Lis and C. J. Milios, *RSC Adv.*, 2013, **3**, 13214; (c) A. B. Canaj, L. E. Nodaraki, K. Slepokura, M. Siczek, D. I. Tzimopoulos, T. Lis and C. J. Milios, *RSC Adv.*, 2014, **4**, 23068.
- 9 M. Llunell, D. Casanova, J. Girera, P. Alemany and S. Alvarez, SHAPE, version 2.0, Barcelona, Spain 2010.
- 10 L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092.
- 11 (a) N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.* 2003, **125**, 8694; (b) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Mart-Gastaldo, A. Gaita-Arino, *J. Am. Chem. Soc.* 2008, **130**, 8874; (c) G. Zhou, T. Han, Y.-Song Ding, N. F. Chilton, and Y.-Zhen Zheng, *Chem. Eur. J.* 2017, **23**, 1;
- 12 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164.
- 13 (a) M. A. Palacios, A. J. Mota, J. E. Perea-Buceta, F. J. White, E. K. Brechin and E. Colacio, *Inorg. Chem.*, 2010, **49**, 10156; (b) Y. -B. Jiang, H.-Z. Kou, R.-J. Wang, A.-L. Cui and J. Ribas, *Inorg. Chem.* 2005, **44**, 709; (c) G. N. Newton, H. Sato, T. Shiga and H. Oshio, *Dalton Trans.*, 2013, **42**, 6701; (d) R. T. W. Scott, L. F. Jones, I. S. Tidmarsh, B. Breeze, R. H. Laye, J. Wolowska, D. J. Stone, A. Collins, S. Parsons, W. Wernsdorfer, G. Aromi, E. J. L. McInnes and E. K. Brechin, *Chem.-Eur.J.*, 2009, **15**, 12389; (e) S. Worl, H. Pritzkow, I. O. Fritsky and R.Kramer, *Dalton Trans*, 2005, **0**, 27.
- 14 (a) T.N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti and E.K.Brechin, *Angew.Chem.,Int.Ed.*, 2012, **51**, 4633; (b) L. Zhao, J. Wu, H. Ke and J. Tang, *Inorg.Chem.*, 2014, **53**, 3519; (c) A. N. Georgopoulou, R. Adam, C. P. Raptopoulou, V. Psycharis, R. Ballesteros, B. Abarca and A. K. Boudalis, *Dalton Trans.*, 2010, **39**, 5020.
- 15 See, for example, the following: (a) J.-P. Sutter, S. Dhers, R. Rajamani, S. Ramasesha, J.-P. Costes, C. Duhayon and L. Vendier, *Inorg. Chem.* 2009, **48**, 5820; (b) C. G. Efthymiou, A. N. Georgopoulou, C. Papatriantafyllopoulou, A. Terzis, C. P. Raptopoulou, A. Escuer and S. P. Perlepes, *Dalton Trans.* 2010, **39**, 8603; (c) Y. Yukawa, G. Aromi, S. Igarashi, J. Ribas, S. A. Svyagin and J. Krzystek, *Angew. Chem., Int. Ed.* 2005, **44**, 1997.
- 16 S. K. Singh, M. F. Beg and G. Rajaraman, *Chem. Eur. J.* 2016, **22**, 672;
- 17 C. G. Efthymiou, T. C. Stamatatos, C. Papatriantafyllopoulou, A. J. Tasiopoulos, W. Wernsdorfer, S. P. Perlepes and G. Christou, *Inorg. Chem.* 2010, **49**, 9737.
- 18 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford Univ. Press, 2006
- 19 R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. McInnes, L. F. Chibotaru and R. E. Winpenny, *Nat. Chem.*, 2013, **5**, 673.
- 20 S.-Y. Lin, L. Zhao, Y.-N. Guo, P. Zhang, Y. Guo and J. Tang, *Inorg. Chem.*, 2012, **51**, 10522.
- 21 N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny and A. Soncini, *Nat. Commun.*, 2013, **4**, 2551.
- 22 S.-D Jiang and S-X. Qin, *Inorg. Chem. Front.*, 2015, **2**, 613.

Heterometallic lanthanide-centred $[\text{Ni}_6\text{Ln}^{\text{III}}]$ rings

Angelos B. Canaj, Demetrios I. Tzimopoulos, Dimitris A. Kalofolias, Milosz Siczek, Tadeusz Lis, Mark Murrie and Constantinos J. Milios

The syntheses, structures and magnetic properties of three new hetero-heptametallic $[\text{Ni}_6\text{Ln}]$ complexes are reported.

