

Dalton Transactions

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.



Slight Synthetic Changes Eliciting Different Topologies: Synthesis, Structure and Magnetic Properties of Novel Dinuclear and Nonanuclear Dysprosium Complexes

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

DOI: 10.1039/x0xx00000x

Che-Jung Kuo,^a Rebecca J. Holmberg,^b and Po-Heng Lin^{*a}

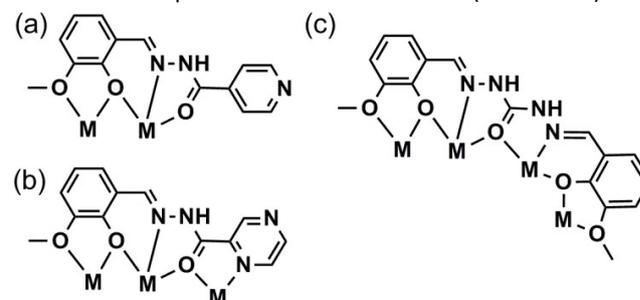
www.rsc.org/dalton

Using the Schiff-base ligand, 1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H₂hmc), generates dinuclear and nonanuclear compounds, [Dy₂(Hhmc)₂(NO₃)₄]·THF·MeCN (1) and [Dy₉(μ₃-O)₄(μ-OH)₆(hmc)₄(NO₃)₄(DMF)₄](OH)·H₂O·THF·DMF (2), respectively, through the addition of different bases. Single-crystal X-ray diffraction analysis revealed a unique Dy₉ core structure of complex 2 and the magnetic properties of both compounds are fully studied.

Lanthanide-based metal clusters have been of increasing interest due to their fascinating structural diversity as well as their electronic, optical, and catalytic properties.¹ In particular, cluster chemistry based on paramagnetic ions has received considerable research interest regarding magnetic properties, especially as Single-Molecule Magnets (SMMs).² Understanding the correlation between structural models and physical properties will offer more information for designing new SMMs. For example, the effect of electron-withdrawing ligands on the energy barriers of SMMs has been investigated through a series of dinuclear complexes with a similar core structure, but different counter ions.³ Moreover, self-assembly of nanoscale high-nuclearity metal clusters via methods of coordination chemistry has been a challenging task which led to the supermolecular assemblies exhibiting novel structural characteristics.⁴ The synthesis of high-nuclearity pure lanthanide clusters with novel topologies continues to be a challenge due to the variable and high coordination numbers, as well as poor directionality inherent to lanthanide ions.⁵ To the best of our knowledge, all nonanuclear lanthanide compounds published thus far have been diabolo shape (or sandglass shape)⁶ where the clusters assemble in two square

pyramidal pentanuclear units via the apical metal center lanthanide ion. Besides their magnetic properties, nonanuclear lanthanide compounds have also shown photosensitized luminescence^{6b, 6h} and optical Faraday effects.^{6d} Thus, lanthanide clusters have many interesting properties yet to be fully explored.

Ligands play an important role in lanthanide cluster syntheses. Polydentate Schiff-base ligands derived from *o*-vanillin have been widely applied for the syntheses of multinuclear lanthanide clusters. Polynuclear lanthanide clusters ranging from dinuclear to dodecanuclear have been synthesized using this ligand system, which provides O- and N-based multi-chelating sites for lanthanide ion complex formation.⁷ Increasing the denticities of the ligands may be one of the most successful strategies toward forming high-nuclearity lanthanide complexes. For example, dinuclear complexes were obtained by using (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine (H₂hmi) (Scheme 1a).^{7e} Designing pyrazine groups in place of pyridine groups offered an additional N atom for metal chelation (Scheme 1b) and penta-⁷ⁱ, hexa-^{7j} and octa^{7k}-nuclear complexes have also been synthesized. With this in mind, the ligand, 1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H₂hmc)⁸, synthesized via condensation of carbonohydrazide and *o*-vanillin was chosen due to the four potential coordination sites (Scheme 1c).



Scheme 1. Coordination modes of (a) (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine (H₂hmi), (b) (2-hydroxy-3-methoxy-benzylidene)pyrazine-2-carbo-hydrazide and (c) 1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H₂hmc).

^a Department of Chemistry, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan. Email: po-heng@nchu.edu.tw; Tel: + 886-4-22840411, ext. 724.

^b Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie-Curie, Ottawa, ON, Canada K1N 6N5.

† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic and additional SQUID data. CCDC 1412245 (1) and 1412246 (2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

COMMUNICATION

Journal Name

Herein, we report the syntheses, structures, and magnetic properties of a novel dinuclear and nonanuclear Dy^{III} clusters which were synthesized by simply altering the basicity of the reaction conditions.

To a solution of Dy(NO₃)₃·6H₂O (0.50 mmol) in MeCN (15ml) was added a solution of H₂hmc (0.25 mmol) and pyridine (0.080 ml, 1.0 mmol) in THF (15 ml). The resulting pale yellow solution gave well-formed pale green crystals in 62% (0.1082 g) yield. The structure of the dinuclear complex, [Dy₂(Hhmc)₂(NO₃)₄]·THF·MeCN (**1**), crystallized in the triclinic *P*-1 space group (Fig. 1).

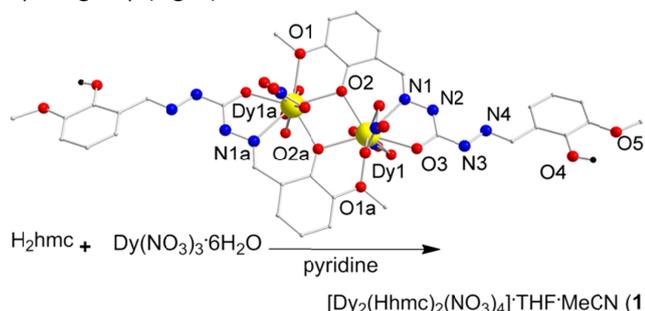


Fig. 1. Molecular structure of complex **1**. Colour code: Dy (yellow), O (red), N (blue) and C (gray). H atoms were omitted for clarity.

The tetradentate ligand coordinates to the Dy centers in the dinuclear unit *via* three O atoms (O1, O2 and O3) and one N1 atom. The metal centers are bridged by the phenoxide groups of two ligands with a Dy-O-Dy angle of 104.14(7)°. The Dy-Dy distance is 3.7076(4) Å. Both Dy^{III} ions are nine coordinate and the remaining four coordination sites of each lanthanide ion are filled by two nitrate anions. The Dy centers are in a distorted pentagonal, interpenetrating tetrahedral arrangement where four oxygen atoms of two nitrates form a distorted tetrahedral position which is interpenetrated by the pentagonal plane of N1, O2, O3, O1a and O2a from Hhmc. Charge balance considerations for the molecule indicate that the ligand must have one negative charge resulting from the ligand being in the keto-form, and one deprotonated O2 atom which is different from the similar dinuclear complexes synthesized with the H₂hmi ligand^{7e} (Fig. S1).

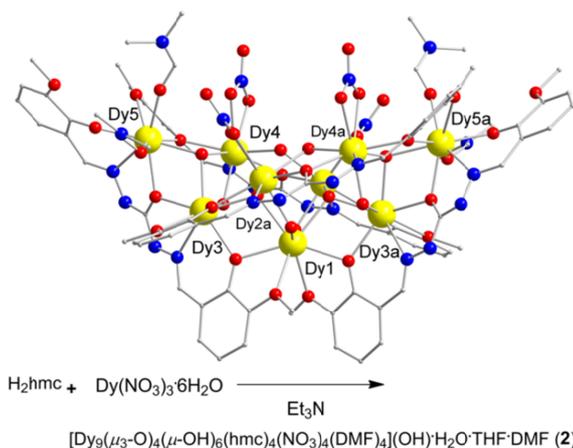


Fig. 2. Molecular structure of complex **2**. Color code: Dy (yellow), O (red), N (blue) and C (gray). H atoms were omitted for clarity.

Since not all potential coordination sites of H₂hmc were occupied in complex **1**, we added NEt₃ instead of pyridine in the reaction which promotes full deprotonation of H₂hmc (H on O4). A suspension of Dy(NO₃)₃·6H₂O (0.282 g, 0.616 mmol) and H₂hmc (0.098 g, 0.274 mmol) in THF/DMF (5:1 ratio) was treated with 3.65 mmol of Et₃N. The resulting yellow solution yielded rectangular, light yellow crystals of the nonanuclear complex [Dy₉(μ₃-O)₄(μ-OH)₆(hmc)₄(NO₃)₄(DMF)₄](OH)·H₂O·THF·DMF (**2**) in 17.9% yield after one week. No crystals were obtained without an excess of base since the deprotonation of H₂O into μ₃-O and μ-OH was linked to Dy^{III} ions. Complex **2** crystallizes in the monoclinic C2/C space group and the structure is composed of nine Dy^{III} ions which are all eight coordinate. (Fig. 2) The ligands coordinated with Dy^{III} in two different coordination modes where four Dy^{III} ions (Dy3a, Dy2, Dy4 and Dy5) were held together by η²:η³:η³:η²-hmc²⁻ and three Dy^{III} atoms (Dy1, Dy3 and Dy5) were linked by η²:η³:η³-hmc²⁻ (Fig. 3).

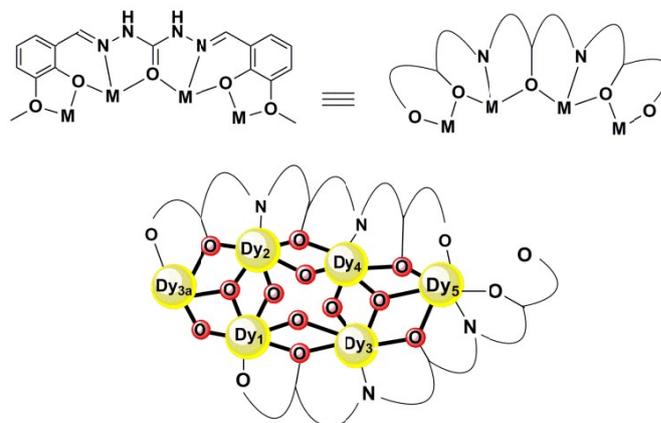


Fig. 3. Representation of the core structure highlighting the coordination modes of the ligands.

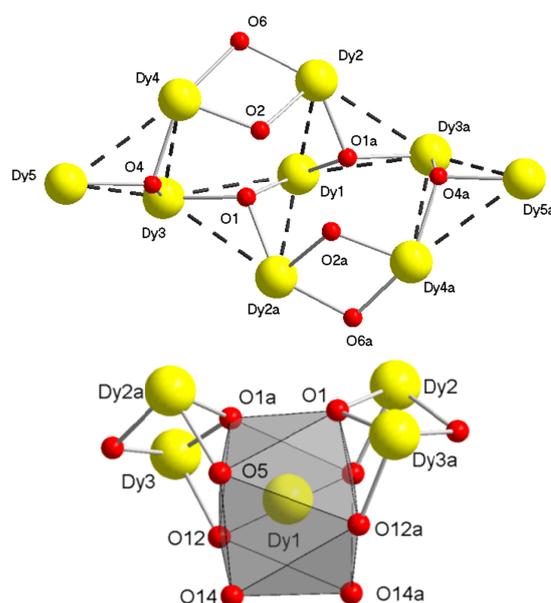


Fig. 4. Top: Representation of the core structure highlighting the triangular subunits in dashed lines. Bottom: Polyhedral representation of Dy1 center with the distorted square-antiprism. Color code: Dy (yellow), O (red).

The metal skeleton can be regarded as four Dy triangles fused in a vertex-sharing fashion and all the triangles are capped by four μ_3 -O atoms (O1, O1a, O4 and O4a) (Fig. 4, top). The nonanuclear complex can be viewed as two pentanuclear fragments which are assembled via the apical metal (Dy1) through two μ_3 -O (O1 and O1a), two μ -OH (O5 and O5a) and two phenoxy oxygen atoms (O12 and O12a). The remaining coordination sites of Dy1 are filled by two methoxy groups of the ligands (O14 and O14a), thus causing Dy1 to adopt a distorted square antiprism geometry (Fig. 4, bottom). The asymmetric unit, $[\text{Dy}_5(\mu_3\text{-O})_2]$, can be regarded as vertex-sharing triangle units assembled via a metal ion, Dy3. In addition, two oxygen atoms (O2 is hydroxide and O6 is the carbonyl group of the ligand) were bridged between Dy2 and Dy4. All Dy atoms are eight coordinate and the rest of the coordination sites are filled by four DMF and four nitrite molecules. It should be mentioned that the coordination environment of Dy2, Dy3 and Dy4 centres are distorted dodecahedra, while Dy5 centres are distorted square antiprisms. (Fig. S2) For charge balance considerations, one hydroxide counter ion has been assigned which is common for nonanuclear lanthanide complexes.^{6b, 6g}

The temperature dependence of the dc magnetic susceptibility (1.8 - 300 K) was measured under an applied dc field of 1000 Oe. The χT vs. T plot (Fig. 5). The room temperature values of the χT products for complexes **1** and **2** were 27.80 and 124.58 $\text{cm}^3\text{Kmol}^{-1}$, respectively. The theoretical spin only value for a single Dy^{III} ion is 14.17 $\text{cm}^3\text{Kmol}^{-1}$ ($^6\text{H}_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$), and thus are 28.39 and 127.53 $\text{cm}^3\text{Kmol}^{-1}$ for two and nine Dy^{III} ions, respectively, which are both near the experimental values observed. The decrease at low temperature can be attributed to antiferromagnetic interactions between Dy^{III} ions, the thermal depopulation of crystal field states, and/or magnetic anisotropy arising from the Dy^{III} ions, where the χT values of complexes **1** and **2** drop to 9.49 and 81.36 $\text{cm}^3\text{Kmol}^{-1}$ at 1.8 K, respectively.

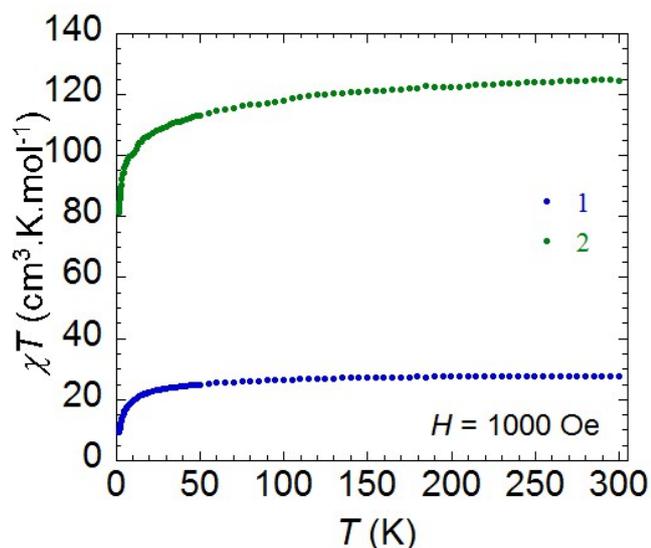


Fig. 5. Temperature dependence of the χT product of complexes **1** and **2** at 1000 Oe.

The isotherm magnetisation (M) measurements (Fig. S3 and S4 for complexes **1** and **2**, respectively) below 7 K reveal a rapid increase in magnetization at low magnetic fields. Above 1.5 T a more gradual increase is observed for both complexes, reaching near saturation at low temperatures ($M = 10.33$ and $41.88 \mu_B$ at 1.8 K under 5 and 7 T, respectively). This behavior displays the presence of magnetic anisotropy within the system which is expected for Dy^{III} . This is further confirmed in Fig. S2 and S3, where the nonsaturation and non-superposition of isotherm lines was apparent in the reduced magnetisation plots at indicated temperatures for both complexes.

The magnetic relaxation dynamics of both complexes were probed by alternating current (ac) magnetic susceptibility measurements. In the literature,^{7e} similar dinuclear Dy complexes observed SMM properties with remarkably large energy barriers, however, complex **1** instead displayed a tail in the out-of-phase (χ'') signal at low temperature under an 1000 Oe applied dc field, with no signal obtained under zero applied dc field. This observation can be explained by two possible reasons: (i) the ferromagnetic interaction between Dy^{III} ions of the aforementioned literature complexes was not observed in the dc magnetic measurements of complex **1**, resulting in a lower spin ground state (S), or (ii) the different core geometries of Dy^{III} ions in complex **1** result in weaker or non-collinear anisotropy axes. Overall, the magnetostructural correlation of bridged dinuclear lanthanide complexes needs to be understood by comparing more lanthanide dinuclear complexes or through further theoretical calculation.

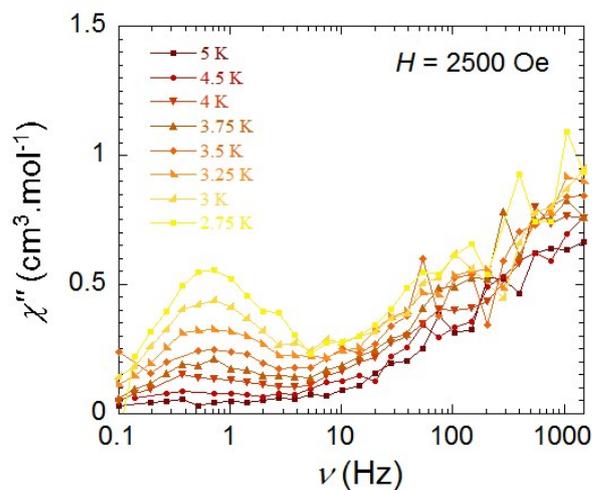


Fig. 6. Frequency dependence of the out-of-phase (χ'') susceptibility of complex **2** under a 2500 Oe applied dc field.

For complex **2**, a tail in the out-of-phase (χ'') signal was observed at low temperature under zero applied dc field. Thus, find-field experiments were performed in order to elucidate the optimal field for observation of a visible peak. Under a 2500 Oe applied dc field a signal was observed for a low-frequency (slow) relaxation process (Fig. 6 and S5) Since an applied dc field was necessitated in order to observe a peak, and that peak is not frequency-dependent, quantum

tunnelling of the magnetization was most likely leading to fast relaxation dynamics at zero-field and under applied fields. Since Dy^{III} has a half-integer spin, as well as significant inherent anisotropy, the absence of slow relaxation dynamics most likely is due to mixing between ground and thermally accessible excited electronic states.

Similarly within the literature there are Dy₅ complexes⁷ⁱ which also possess a core with two Dy triangles fused in a vertex-sharing fashion, which is similar to the subunit of complex **2**. These complexes have been shown to exhibit slow relaxation of magnetization. However, there is no out-of-phase ac signal noticed for complex **2**. This correlation was also observed between Dy₅ complexes with a square pyramidal unit⁹ and Dy₉ complexes with diabolo-shaped core.^{6b, 6g} Indeed, the structural differences clearly affect the anisotropy of each Dy site and their respective orientations. Here we presented another example of a head-to-head arrangement of two SMM units in Dy₉ which presumably cancelled the net anisotropy of the units and lead to the absence of slow relaxation.

Conclusions

Treating the ligand, H₂hmc, with an appropriate base can cause deprotonation to one or two phenoxides leading to dinuclear and nonanuclear dysprosium complexes. The dinuclear core is similar to complexes found within the literature, however, complex **1** is not a SMM. The novel nonanuclear Dy^{III} core of complex **2** was assembled by two unique pentanuclear units via the apical metal center. This metal cluster will offer a new model for further mechanistic studies related to SMM properties or other physical properties of multi-nuclear lanthanide chemistry.

Acknowledgment

This work was supported by National Chung Hsing University and the financial support from the Ministry of Science and Technology, Taiwan (MOST 101-2113-M-033-008-MY3).

Notes and references

- (a) J.-C. G. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897; (b) A. Muller and P. Gouzerh, *Chem. Soc. Rev.*, 2012, **41**, 7431; (c) S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189.
- (a) M. Murrie, *Chem. Soc. Rev.*, 2010, **39**, 1986; (b) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110; (c) F. Habib and M. Murugesu, *Chem. Soc. Rev.*, 2013, **42**, 3278.
- F. Habib, G. Brunet, V. Vieru, I. Korobkov, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2013, **135**, 13242.
- (a) G. Schmid, M. Baumle, M. Geerkens, I. Heim, C. Osemann and T. Sawitowski, *Chem. Soc. Rev.*, 1999, **28**, 179; (b) B. K. Teo and N. J. A. Sloane, *Inorg. Chem.*, 1985, **24**, 4545; (c) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334; (d) G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418; (e) U. Schubert, *Chem. Soc. Rev.*, 2011, **40**, 575.
- (a) M. Y. Wu, F. L. Jiang, X. J. Kong, D. Q. Yuan, L. S. Long, S. A. Al-Thabaiti and M. C. Hong, *Chem. Sci.*, 2013, **4**, 3104; (b) X.-J. Kong, Y. Wu, L.-S. Long, L.-S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 6918; (c) L. Chen, J.-Y. Guo, X. Xu, W.-W. Ju, D. Zhang, D.-R. Zhu and Y. Xu, *Chem. Commun.*, 2013, **49**, 9728.
- (a) M. Addamo, G. Bombieri, E. Foresti, M. D. Grillone and M. Volpe, *Inorg. Chem.*, 2004, **43**, 1603; (b) D. I. Alexandropoulos, S. Mukherjee, C. Papatriantafyllopoulou, C. P. Raptopoulou, V. Psycharis, V. Bekiari, G. Christou and T. C. Stamatatos, *Inorg. Chem.*, 2011, **50**, 11276; (c) J. F. Greisch, M. E. Harding, B. Schafer, M. Ruben, W. Klopfer, M. M. Kappes and D. Schooss, *J. Phys. Chem. Lett.*, 2014, **5**, 1727; (d) T. Nakanishi, Y. Suzuki, Y. Doi, T. Seki, H. Koizumi, K. Fushimi, K. Fujita, Y. Hinatsu, H. Ito, K. Tanaka and Y. Hasegawa, *Inorg. Chem.*, 2014, **53**, 7635; (e) M. A. Singh-Wilmot, R. A. Sinclair, M. Andrews, C. Rowland, C. L. Cahill and M. Murugesu, *Polyhedron*, 2013, **53**, 187; (f) G. Xu, Z. M. Wang, Z. He, Z. Lu, C. S. Liao and C. H. Yan, *Inorg. Chem.*, 2002, **41**, 6802; (g) X. B. Xu, L. Zhao, G. F. Xu, Y. N. Guo, J. K. Tang and Z. L. Liu, *Dalton. Trans.*, 2011, **40**, 6440; (h) B. Zhang, T. Xiao, C. M. Liu, Q. Li, Y. Y. Zhu, M. S. Tang, C. X. Du and M. P. Song, *Inorg. Chem.*, 2013, **52**, 13332.
- (a) X. Yang, R. A. Jones and W.-K. Wong, *Dalton. Trans.*, 2008, 1676; (b) H. Tian, Y.-N. Guo, L. Zhao, J. Tang and Z. Liu, *Inorg. Chem.*, 2011, **50**, 8688; (c) H. Ke, G.-F. Xu, L. Zhao, J. Tang, X.-Y. Zhang and H.-J. Zhang, *Chem. Eur. J.*, 2009, **15**, 10335; (d) L. Zhao, S. Xue and J. Tang, *Inorg. Chem.*, 2012, **51**, 5994; (e) P.-H. Lin, T. J. Burchell, R. Clérac and M. Murugesu, *Angew. Chem. Int. Ed.*, 2008, **47**, 8848; (f) S. Xue, L. Zhao, Y.-N. Guo, P. Zhang and J. Tang, *Chem. Commun.*, 2012, **48**, 8946; (g) V. Chandrasekhar, S. Hossain, S. Das, S. Biswas and J.-P. Sutter, *Inorg. Chem.*, 2013, **52**, 6346; (h) P.-H. Lin, T. J. Burchell, L. Ungur, L. F. Chibotaru, W. Wernsdorfer and M. Murugesu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9489; (i) H. Tian, L. Zhao, H. Lin, J. Tang and G. Li, *Chem. Eur. J.*, 2013, **19**, 13235; (j) H. Tian, M. Wang, L. Zhao, Y.-N. Guo, Y. Guo, J. Tang and Z. Liu, *Chem. Eur. J.*, 2012, **18**, 442; (k) H. Tian, L. Zhao, Y.-N. Guo, Y. Guo, J. Tang and Z. Liu, *Chem. Commun.*, 2012, **48**, 708.
- M. M. Sow, O. Diouf, M. Seck, A. H. Barry and M. Gaye, *Acta. Cryst. E.*, 2014, **70**, o423.
- M. T. Gamer, Y. Lan, P. W. Roesky, A. K. Powell and R. Clérac, *Inorg. Chem.*, 2008, **47**, 6581.