



Myo-inositol supported heterometallic Dy₂₄M₂ (M = Ni, Mn) cages[†]

Cite this: *CrystEngComm*, 2014, 16, 5527

Received 19th February 2014,
Accepted 30th April 2014

DOI: 10.1039/c4ce00362d

www.rsc.org/crystengcomm

Da-Peng Liu, Jun-Bo Peng, Xin-Ping Lin, Que Huang, Xiang-Jian Kong,*
La-Sheng Long,* Rong-Bin Huang and Lan-Sun Zheng

Two heterometallic cage-like Dy₂₄M₂ (M = Ni, Mn) cluster compounds have been synthesized through self-assembly of the metal ions and myo-inositol ligand templated by three ClO₄⁻ anions.

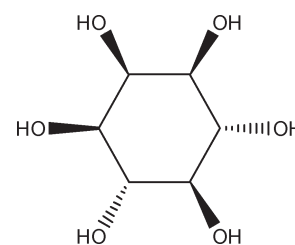
Recently, considerable research in coordination chemistry is focused on the synthesis and investigation of heterometallic 3d–4f polynuclear compounds owing to their fascinating architecture and their potential applications in a number of research fields, including biology, materials science, and magnetism.^{1–5} Up to now, a great variety of low-nuclearity 3d–4f compounds have been realized.^{6,7} However, high-nuclearity heterometallic 3d–4f clusters, especially including more than 20 metal ions, are rare, because of the repulsion of high positive charges of metal ions and the competitive reactions between 3d and 4f metals chelating to the same ligand.^{8–10}

Recent studies have revealed that the anion template strategy is an effective approach to increase the nuclearity of heterometallic clusters, due to the dispersion action of the anion template for the positive charge of clusters.^{11–13} Over the course of these investigations, the use of a simple single anion as a template has been studied most extensively. However, compared with the single anion template, the multiple anions template would be a better approach to construct high-nuclearity 3d–4f metal clusters, because of the multiple anions template dispersion action for the positive charge of clusters.¹¹

Polyalcohol ligands are the favorite candidate for the synthesis of polynuclear 3d–4f clusters, and many polynuclear clusters have been constructed from polyalcohol ligands, such as single-molecule magnets (SMMs) of Mn–4f

clusters.¹⁴ Because of possessing six hydroxyl groups,¹⁵ myo-inositol was selected to construct high-nuclearity metal clusters in this work (Scheme 1). Two high-nuclearity heterometallic 3d–4f clusters, formulated as [Dy₂₄M₂(OH)₈(CH₃COO)₁₂(C₆H₁₀O₆)₆(C₆H₉O₆)₆(H₂O)₅₁][Dy(H₂O)₉](ClO₄)₂₉·(H₂O)₈₀·(C₂H₅OH)₄ (M = Ni for 1; M = Mn for 2), were synthesized based on the myo-inositol ligand.[‡] Structural analysis shows that three ClO₄⁻ anions, acting as templates, are located in the cage of the clusters. Compounds 1 and 2 were obtained from the reaction of Dy(ClO₄)₃, M(CH₃COO)₂, myo-inositol, and NaOH in a 10 mL mixture of anhydrous ethanol. They were found to be isomorphous, as revealed by single-crystal X-ray diffraction studies. As a representative, the structure of 1 is discussed to illustrate the structural features common to the two compounds. The cationic cluster of [Dy₂₄M₂(OH)₈(CH₃COO)₁₂(C₆H₁₀O₆)₆(C₆H₉O₆)₆(H₂O)₅₁]²⁶⁺ features a cage structure that encapsulates three ClO₄⁻ anions, as shown in Fig. 1.

The cage-like cluster core of 1 can be viewed as being constructed from two [Dy₉Ni(OH)₄(CH₃COO)₆(C₆H₁₀O₆)₃(C₆H₉O₆)₃(H₂O)₁₅]⁴⁺ units and three [Dy₂(H₂O)₇]⁶⁺ units (Fig. 2). As shown in Fig. 2b, each [Dy₉Ni(OH)₄(CH₃COO)₆(C₆H₁₀O₆)₃(C₆H₉O₆)₃(H₂O)₁₅]⁴⁺ unit is made up of one [Dy₉Ni(OH)₄]²⁵⁺ core, six acetates, three [C₆H₁₀O₆]²⁻ and three [C₆H₉O₆]³⁻ anions, and fifteen aqua ligands. The [Dy₉Ni(OH)₄]²⁵⁺ core can be viewed as three [Dy₃OH]⁸⁺ ions connected by one OH⁻ and one Ni²⁺ ion (Fig. 2c). The adjacent [Dy₃OH]⁸⁺ units are also connected by one [C₆H₉O₆]³⁻ ligand, which links four Dy³⁺ and one Ni²⁺ in



Scheme 1 The myo-inositol ligand.

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: xjkong@xmu.edu.cn, lslong@xmu.edu.cn

[†] Electronic supplementary information (ESI) available: Details of synthesis of 1 and 2, crystal data, Tables S1–S3, and Fig. S1–S12. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00362d

a $\mu_5:\eta^1:\eta^2:\eta^3:\eta^2:\eta^1:\eta^0$ fashion (Fig. S1[†]), forming a $[\text{Dy}_9\text{Ni}(\text{OH})_4(\text{C}_6\text{H}_9\text{O}_6)_3]^{16+}$ unit. The $[\text{Dy}_9\text{Ni}(\text{OH})_4(\text{C}_6\text{H}_9\text{O}_6)_3]^{16+}$ unit is further coordinated by 6 acetates, 15 aqua ligands and three $[\text{C}_6\text{H}_{10}\text{O}_6]^{2-}$ ligands, resulting in the bowl-like structure of $[\text{Dy}_9\text{Ni}(\text{OH})_4(\text{CH}_3\text{COO})_6(\text{C}_6\text{H}_{10}\text{O}_6)_3(\text{C}_6\text{H}_9\text{O}_6)_3(\text{H}_2\text{O})_{15}]^{4+}$. The cage-like cluster core is made up of two bowl-like units linked by three $[\text{Dy}_2(\text{H}_2\text{O})_7]^{6+}$ units through the coordination of three $[\text{C}_6\text{H}_{10}\text{O}_6]^{2-}$ ligands, which bridge four Dy^{3+} ions in a $\mu_4:\eta^1:\eta^2:\eta^1:\eta^1:\eta^2:\eta^1$ fashion (Fig. S1[†]). Structural analysis shows that the polyalcohol is a better candidate ligand to

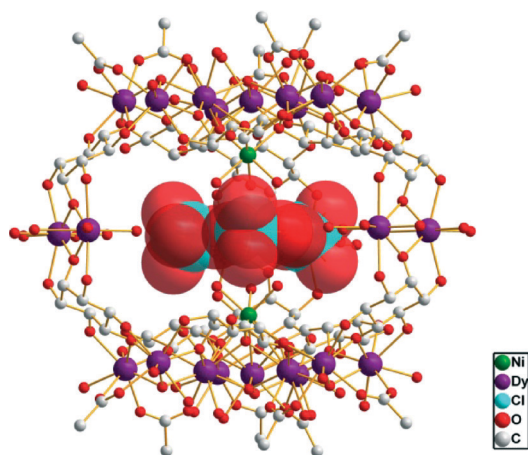


Fig. 1 (a) Ball-and-stick view of the cationic $\text{Dy}_{24}\text{Ni}_2$ cluster in **1** along the *a* axis.

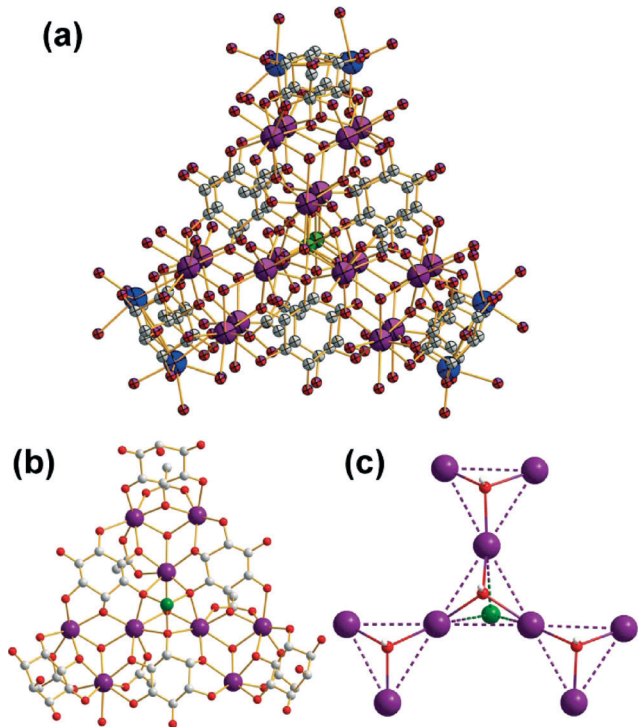


Fig. 2 Ball-and-stick view of the cationic $\text{Dy}_{24}\text{Ni}_2$ core of **1** along the *c* axis (a), the structure of the $[\text{Dy}_9\text{Ni}(\text{OH})_4(\text{CH}_3\text{COO})_6(\text{C}_6\text{H}_{10}\text{O}_6)_3(\text{C}_6\text{H}_9\text{O}_6)_3(\text{H}_2\text{O})_{15}]^{4+}$ unit (b) and the structure of the $[\text{Dy}_9\text{Ni}(\text{OH})_4]$ unit (c). Purple and blue for Dy, green for Ni, red for O, and grey for C.

construct high-nuclearity 3d–4f metal clusters. Three templating ClO_4^- anions are found in the center of the cage.

Each of the $\text{Ni}^{2+}/\text{Mn}^{2+}$ ions is hexa-coordinated by six O atoms, three O from $[\text{C}_6\text{H}_{10}\text{O}_6]^{3-}$ and three O from three aqua ligands, displaying distorted octahedral coordination geometry. Dy1, Dy2, Dy3 and Dy4 are octa-coordinate and form bicapped trigonal prism geometry; Dy5 is hepta-coordinate, while Dy6 is nona-coordinate (Fig. S2[†]). The Ni1/Mn1 and Cl1 atoms lie on a threefold axis. Dy4 and Dy5 lie on mirror planes, while the Dy6 atom of the $[\text{Dy}(\text{H}_2\text{O})_9]$ species lies at a site with bar-6 symmetry. The Dy–O distances range from 2.250(8) to 2.541(12) Å, and the Ni–O distances are in the range of 2.062(7)–2.127(7) Å, which are comparable to those in the reported compounds.¹⁶ The Dy···Dy and Dy···Ni separations are 3.760(1)–3.905(1) Å and 3.491(2) Å, respectively.

The temperature-dependent magnetic susceptibilities of the crystalline samples of compounds **1** and **2** were investigated between 2 K and 300 K under a direct-current (DC) field of 1 kOe, as shown in Fig. 3. At 300 K, the $\chi_{\text{M}}T$ value is $357.4 \text{ cm}^3 \text{ K mol}^{-1}$ (calcd. $356.25 \text{ cm}^3 \text{ K mol}^{-1}$ for 25 Dy^{3+} ions with $S = 5/2$, ${}^6\text{H}_{15/2}$, $g = 4/3$ and 2 Ni^{2+} with $S = 1$, $g = 2.0$) for **1** and $358.7 \text{ cm}^3 \text{ K mol}^{-1}$ (calcd. $358.63 \text{ cm}^3 \text{ K mol}^{-1}$ for 25 Dy^{3+} ions with $S = 5/2$, ${}^6\text{H}_{15/2}$, $g = 4/3$ and 2 Mn^{2+} with $S = 5/2$, $g = 2.0$) for **2**. $\chi_{\text{M}}T$ decreases gradually with the decrease of temperature from 300 to 100 K and then falls abruptly down to the value of $238.2 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** and $297.0 \text{ cm}^3 \text{ K mol}^{-1}$ for **2** at 2 K. The decrease of the $\chi_{\text{M}}T$ curve is attributed to a combination of intramolecular antiferromagnetic interactions and depopulation of Stark sublevels of the Dy^{3+} ions.¹⁷

The field dependence of magnetization of compounds **1** and **2** is shown in Fig. S6[†]. The magnetization at 2 K increases very fast below 1 T, and then slowly and linearly increases and is even saturated at 7 T. The maximum values of M are $141.1 \mu_{\text{B}}$ for **1** and $155.8 \mu_{\text{B}}$ for **2** at 7 T, which are smaller than the expected values for 25 ferromagnetically aligned Dy^{3+} ions and 2 $\text{Ni}^{2+}/\text{Mn}^{2+}$, suggesting the presence of significant anisotropy and/or low-lying excited states.⁷

In order to investigate the dynamics of these systems, alternating current susceptibilities were performed. As shown in Fig. 4, the out-of-phase components of **1** and **2** are strongly

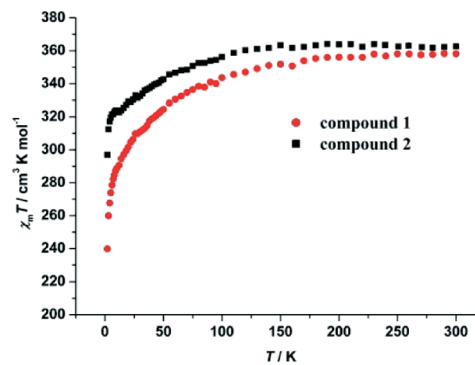


Fig. 3 Plots of the temperature dependence of $\chi_{\text{M}}T$ of **1** and **2** under a 1000 Oe field between 2 and 300 K.

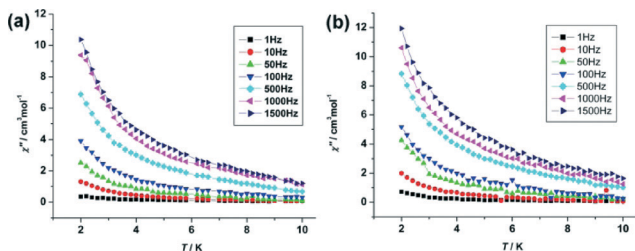


Fig. 4 Temperature dependence of the out-of-phase (χ'') components of the ac susceptibilities of **1** and **2** at different ac frequencies and under a zero DC field.

frequency-dependent, indicating the slow magnetic relaxation. However, because of the absence of frequency-dependent peaks in out-of-phase susceptibility signals, the energy barrier and the characteristic relaxation time of the system cannot be obtained by fitting the peak temperatures to an Arrhenius-type expression. But assuming that there is only one characteristic relaxation process, the energy barrier and τ_0 values can be obtained from the relationship $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_B T$.¹⁸ As shown in Fig. S11 and S12,[†] the calculated values are $E_a = 1.24$ K and $\tau_0 = 5.61 \times 10^{-5}$ s for **1** and $E_a = 0.98$ K and $\tau_0 = 6.67 \times 10^{-5}$ s for **2**.

In conclusion, two heterometallic 3d–4f clusters based on the myo-inositol ligand have been synthesized. The cluster core possesses a fascinating cage-like structure with two $[\text{Dy}_9\text{Ni}(\text{OH})_4]^{25+}$ units and templating three ClO_4^- anions. Magnetic studies revealed that $\text{Dy}_{24}\text{Ni}_2$ and $\text{Dy}_{24}\text{Mn}_2$ display slow relaxation of magnetization. The present work demonstrates the validity of assembly of high-nuclearity 3d–4f metal clusters based on the multiple anions template approach.

Acknowledgements

This work was supported by the 973 project (grant 2012CB821704) from the Ministry of Science and Technology of China, the National Natural Science Foundation of China (grants no. 21371144, 21390390 and 90922031), and the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (201219).

Notes and references

[†] To synthesise **1** and **2**, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (249 mg, 1.0 mmol) for **1** and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (245 mg, 1.0 mmol) for **2**, $\text{Dy}(\text{ClO}_4)_3$ (4 ml, 4.0 mmol) and myo-inositol (180 mg, 1.0 mmol) were added to a mixture of 10 mL of anhydrous ethanol. The resulting solution was heated to about 70 °C and a freshly prepared NaOH solution (aq. 1.0 mol L⁻¹) was added dropwise to adjust the pH of the solution to 6 while stirring. Then, the solution was refluxed for 2 hours and then filtered. Evaporation of the filtrate afforded block-shaped crystals in two weeks with 170 mg (yield 16%) for **1** and 180 mg (yields 17%) for **2**. Anal. calcd(%) for **1**: C, 9.80; H, 3.62; found(%) C, 9.99; H, 3.51. Anal. calcd(%) for **2**: C, 9.81; H, 3.62; found(%) C, 9.88; H, 3.55. Crystallographic data in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 983777 for **1** and 983778 for **2**.

1 (a) A. Mishra, W. Wernsdorfer, K. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 15648; (b) V. Mereacre,

A. M. Ayuk, R. Clérac, W. Wernsdorfer, G. Filoti, J. Bartolomé, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc.*, 2007, **129**, 9248; (c) T. Shiga, T. Onuki, T. Matsumoto, H. Nojiri, G. N. Newton, N. Hoshino and H. Oshio, *Chem. Commun.*, 2009, 3568.

- (a) Y. Z. Zheng, M. Evangelisti and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2011, **50**, 3692; (b) Y. Z. Zheng, M. Evangelisti and R. E. P. Winpenny, *Chem. Sci.*, 2011, **2**, 99.
- (a) F. Gao, L. Cui, Y. Song, Y. Z. Li and J. L. Zuo, *Inorg. Chem.*, 2014, **53**, 562; (b) Y. Liu, Z. Chen, J. Ren, X.-Q. Zhao, P. Cheng and B. Zhao, *Inorg. Chem.*, 2012, **51**, 7433.
- (a) X.-J. Kong, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *Acc. Chem. Res.*, 2009, **43**, 201; (b) L.-F. Zou, L. Zhao, Y.-N. Guo, G.-M. Yu, Y. Guo, J.-K. Tang and Y.-H. Li, *Chem. Commun.*, 2011, **47**, 8659.
- N. F. Chilton, S. K. Langley, B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2010, **46**, 7787.
- (a) V. M. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, G. Filoti, J. Bartolome, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc.*, 2007, **129**, 9248; (b) F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi and H. Nojiri, *J. Am. Chem. Soc.*, 2006, **128**, 1440; (c) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc.*, 2004, **126**, 420; (d) Y.-Z. Zheng, G.-J. Zhou, Z. Zheng and R. E. Winpenny, *Chem. Soc. Rev.*, 2014, **43**, 1462.
- (a) H. Xiang, Y. H. Lan, H. Y. Li, L. Jiang, T. B. Lu, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, **39**, 4737; (b) S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti and K. S. Murray, *Chem. Sci.*, 2011, **2**, 1166; (c) M. Andruh, J. P. Costes, C. Diaz and S. Gao, *Inorg. Chem.*, 2009, **48**, 3342; (d) Y. G. Huang, F. L. Jiang and M. C. Hong, *Coord. Chem. Rev.*, 2009, **253**, 2814; (e) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328.
- (a) Z. M. Zhang, L. Y. Pan, W. Q. Lin, J. D. Leng, F. S. Guo, Y. C. Chen, J. L. Liu and M. L. Tong, *Chem. Commun.*, 2013, **49**, 8081; (b) J. D. Leng, J. L. Liu and M. L. Tong, *Chem. Commun.*, 2012, **48**, 5286.
- (a) X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, T. D. Harris and Z. Zheng, *Chem. Commun.*, 2009, 4354; (b) X. J. Kong, Y. P. Ren, W. X. Chen, L. S. Long, Z. P. Zheng, R. B. Huang and L. S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 2398.
- (a) J. J. Zhang, S. M. Hu, S. C. Xiang, T. L. Sheng, X. T. Wu and Y. M. Li, *Inorg. Chem.*, 2006, **45**, 7173; (b) A. Baniodeh, I. J. Hewitt, V. Mereacre, Y. Lan, G. Novitchi, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2011, **40**, 4080; (c) X. Yang, D. Schipper, R. A. Jones, L. A. Lytwak, B. J. Holliday and S. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 8468.
- (a) J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-Z. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314; (b) 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.
- (a) C. Papatriantafyllopoulou, W. Wernsdorfer, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2011, **50**, 421; (b)

- M. Towatari, K. Nishi, T. Fujinami, N. Matsumoto, Y. Sunatsuki, M. Kojima, N. Mochida, T. Ishida, N. Re and J. Mrozinski, *Inorg. Chem.*, 2013, 52, 6160; (c) X. M. Chen, S. M. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mak and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, 117, 9600.
- 13 L.-F. Zou, L. Zhao, Y.-N. Guo, G.-M. Yu, Y. Guo, J.-K. Tang and Y.-H. Li, *Chem. Commun.*, 2011, 47, 8659.
- 14 (a) J. W. Sharples and D. Collison, *Coord. Chem. Rev.*, 2014, 260, 1; (b) V. Chandrasekhar, P. Bag, M. Speldrich, J. van Leusen and P. Kögerler, *Inorg. Chem.*, 2013, 52, 5035; (c) V. Mereacre, M. N. Akhtar, Y. Lan, A. M. Ako, R. Clerac, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, 39, 4918; (d) A. Saha, M. Thompson, K. A. Abboud, W. Wernsdorfer and G. Christou, *Inorg. Chem.*, 2011, 50, 10476.
- 15 H. Hu, J. Xue, X. Wen, W. Li, C. Zhang, L. Yang, Y. Xu, G. Zhao, X. Bu and K. Liu, *Inorg. Chem.*, 2013, 52, 13132.
- 16 K. C. Xiong, X. Y. Wang, F. L. Jiang, Y. L. Gai, W. T. Xu, K. Z. Su, X. J. Li, D. Q. Yuan and M. C. Hong, *Chem. Commun.*, 2012, 48, 7456.
- 17 (a) C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, 102, 2369; (b) C. Zaleski, E. Depperman, J. Kampf, M. Kirk and V. Pecoraro, *Angew. Chem., Int. Ed.*, 2004, 43, 3912; (c) Z. Majeed, K. C. Mondal, G. E. Kostakis, Y. Lan, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, 39, 4740.
- 18 (a) S. Y. Lin, G. F. Xu, L. Zhao, Y. N. Guo, Y. Guo and J. K. Tang, *Dalton Trans.*, 2011, 40, 8213; (b) J. Bartolomé, G. Filoti, V. Kuncser, G. Schinteie, V. Mereacre, C. E. Anson, A. K. Powell, D. Prodius and C. Turta, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, 80, 014430.