

Synthesis and characterization of decanuclear Ln(III) cluster of mixed calix[8]arene-phosphonate ligands (Ln = Pr, Nd)



Kongzhao Su^{a,b}, Feilong Jiang^a, Jinjie Qian^{a,b}, Jiandong Pang^{a,b}, Falu Hu^{a,b}, Salem M. Bawaked^c, Mohamed Mokhtar^c, Shaeel A. AL-Thabaiti^c, Maochun Hong^{a,*}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

^c Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 17 December 2014

Received in revised form 25 January 2015

Accepted 28 January 2015

Available online 29 January 2015

Keywords:

Calixarenes

Cluster compounds

Photoluminescent properties

Magnetic properties

Lanthanides

ABSTRACT

Two novel decanuclear Ln(III) compounds (Ln = Pr for **1**, Nd for **2**) have been solvothermally obtained by using *p*-tert-butylcalix[8]arene (H₈TBC8A) and phenylphosphonate (PhPO₃H₂) as ligands. Single crystal X-ray diffraction studies reveal that both compounds are stacked by dumbbell-like Ln₁₀ clusters, which are capped by two TBC8A⁸⁻ supports and linked by four complementary PhPO₃²⁻ ligands as well as other bridging anions. In addition, the self-assembly behavior of both compounds is interesting: the cationic Ln₁₀ cluster layers are separated by the layers of H₆TBC8A²⁻ ligands. Moreover, the luminescent and magnetic properties of both compounds were examined.

© 2015 Elsevier B.V. All rights reserved.

The design and construction of high-nuclearity lanthanide (Ln) clusters is one of the most active research frontiers in coordination chemistry, not only due to their aesthetically pleasing structures [1] but also their potential applications including luminescence [2], magnetism [3], catalyst [4] and so on [5]. In recent years, chemists have paid much more attention on constructing polymetallic complexes by using calixarenes [6]. A variety of alkali, transition (TM), or lanthanide metal coordination compounds supported by calixarenes have been obtained so far, especially for thiacalix[4]arenes [7]. However, the number of coordination compounds supported by *p*-tert-butylcalix[8]arene (H₈TBC8A) is relatively less [8]. This might be in part ascribed to the reasons that the H₈TBC8A molecule is limited solubility in most organic solvents, more flexible in comparison to those smaller membered calix[4]arenes and hard to control over stereoselective substitution reactions at the rims, which present many kinds of structural conformations and hence make the large calix[8]arene difficult to arrange in long-range order in the solid state [8d].

On the other hand, phosphate and phosphonate ligands, which possess different anionic forms and thus can adopt various coordination modes, have been confirmed to be excellent ligands for making polymetallic compounds [9]. Very recently, by using these as co-ligands, we have isolated some (thia)calix[4]arene-based high-nuclearity complexes with interesting architectures and properties. For example, we

have synthesized a series of thiacalix[4]arene-based high-nuclearity TM_{4n} nanocages (TM = Co, Ni; n = 2–6) constructed by bridging TM₄-calix[4]arene molecule building blocks (MBBs) with phosphate/phosphonate ligands [10], two calix[4]arene-based Co₉ clusters with an obvious structural change in the metallic skeleton converting from regular tri-capped trigonal prisms to distorted ones by employing auxiliary phosphonate ligands [11], and two alkali-metal templated Na₂Co₂₄ and KCo₂₄ clusters based on thiacalix[4]arene and phosphate ligands [12].

As we know, several compounds with cluster motifs containing 1, 2 and 4–8 Ln centers based on H₈TBC8A have been reported previously by the research groups of Dalgarno and Harrowfield [13]. Therefore, we have attempted to investigate whether it is possible to obtain high-nuclearity clusters by introducing phosphonate ligand into the larger membered calix[8]arene system. Fortunately, we have successfully isolated two novel dumbbell-like decanuclear Ln₁₀ clusters (Ln = Pr, Nd) constructed from the H₈TBC8A and phenylphosphonate ligand under solvothermal conditions (Fig. 1). Herein we report their syntheses, structures, photoluminescent and magnetic properties.

The reaction of Ln(NO₃)₃·6H₂O, H₈TBC8A and PhPO₃H₂ in a basic DMF–CH₃OH mixed solvent (1:1, v/v) at 130 °C produced colorless plate crystals, namely [Pr₁₀(TBC8A)₂(PhPO₃)₄(OH)₂(HCO₃)(HCOO)(DMF)₁₄]·(H₆TBC8A)·2DMF·2CH₃OH (**1**) and [Nd₁₀(TBC8A)₂(PhPO₃)₄(OH)₂(HCO₃)(HCOO)(DMF)₁₄]·(H₆TBC8A)·8CH₃OH (**2**). Single crystal X-ray diffraction experiments reveal that the dumbbell-like Ln^{III}₁₀ cluster houses within two TBC8A⁸⁻ supports and four complementary PhPO₃²⁻ ligands as well as other bridging anions. Up to now, there

* Corresponding author.

E-mail address: hmc@fjirsm.ac.cn (M. Hong).

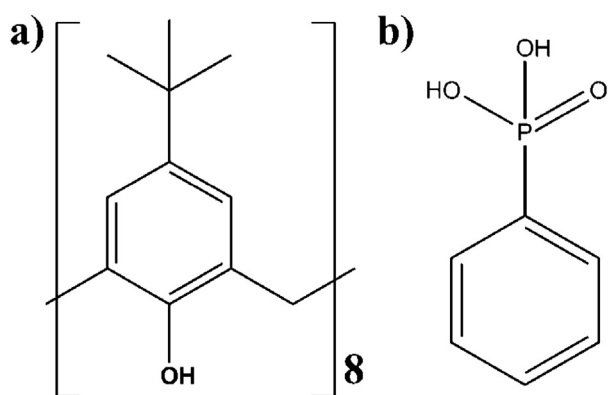


Fig. 1. Ligands used in this paper. (a) The molecule structure of *p*-tert-butylcalix[8]arene (H₈TBC8A); (b) The molecule structure of phenylphosphonate (PhPO₃H₂).

have been few reported decanuclear lanthanide clusters in combinatorial configurations and their cores adopt Z-shaped or plate structures. However, this dumbbell-like architecture here has not been reported so far [14]. Notably, compounds **1** and **2** also represent the largest pure lanthanide aggregates to be formed with H₈TBC8A ligands.

Crystals of title compounds are in triclinic systems and structure solutions are performed in the space group *P*-1. Except the co-crystallized solvents, these two calix[8]arene based clusters are structurally similar, and thus compound **1** is described in detail as representative hereafter. Within the asymmetric unit, there are five crystallographically independent Pr^{III} sites and they can be divided into three types with Pr1, Pr2 and Pr4 being in eight-coordinate O₈ environment, Pr3 nine-coordinate O₉ environment and Pr5 seven-coordinate O₇ environment. Moreover, four Pr^{III} ions (Pr2–Pr5) coordinate to eight lower-rim phenolic oxygens from one fully deprotonated TBC8A⁸⁻ ligand and one central μ₄-OH in the basal plane to form a double-cone tetranuclear praseodymium-calixarene entity (Fig. 2). We note that the protonation levels of central OH⁻ were determined by bond valence sum (BVS) calculations (Table S1, in the Supporting Information). Then, two of the abovementioned double-cone entities are connected in a head-to-head style by one HCOO⁻ anion, one HCO₃⁻ anion, two Pr^{III} ions and four PhPO₃²⁻ ligands, forming a dumbbell-like entity, which is larger than our previous reported smaller membered calix[4]arene-based Ni₈ dumbbell-like entity [15]. It should be noted that one of the bridging anions is HCO₃⁻ rather than CO₃²⁻ in this structure because one of the distances between the carbon

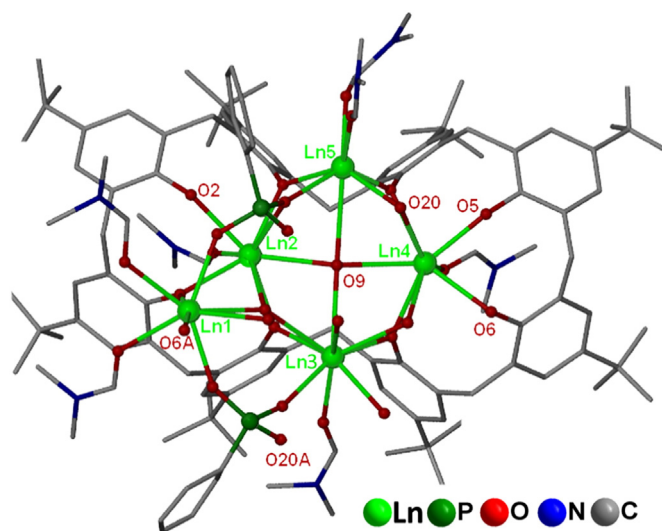


Fig. 2. X-ray asymmetric unit of **1**. Symmetry codes: A 1 - x, 1 - y, -z. The hydrogen atoms and co-crystallized H₆TBC8A²⁻ and solvents are omitted for clarity.

and oxygen atom is much longer than the remaining two distances. The formate anion comes from the decarboxylation of DMF solvent under solvothermal reaction conditions, and the bicarbonate anion originates from the incorporation of atmospheric carbon dioxide. Charge balance is maintained through the deprotonation of two phenolic hydroxyl groups of a cocrystal H₆TBC8A molecule. Moreover, the remaining six unde protonated phenolic hydroxyl groups form six intramolecular hydrogen bonds with the O···O distances ranging from 2.449 to 2.632 Å, which are in agreement with the reported examples [8b]. All auxiliary phosphonate ligands bind to four metal ions in this structure with a 4.112 coordination mode according to Harris notation [16]. Moreover, the distance between the two planes formed by four Pr^{III} ions from the upper and bottom of the dumbbell-like entity is about 5.05 Å. It should be mentioned that the Pr5 metal site and some ligated DMF molecules are disordered (see CIF file for details), and thus we avoid discussing detailed bond lengths and angles of this structure. Due to the additional H₆TBC8A²⁻ anions, the examination of the extended structure of compound **1** is unusual, which contains two different kinds of layers: the Pr₁₀ cluster layer and co-crystallized H₆TBC8A²⁻ layer, as can be seen from Fig. 3. Interestingly, these two different layers are separated by each other leading to sandwich-like arrays via weak interactions. Moreover, the co-crystallized H₆TBC8A²⁻ ligands in this structure adopt pleated-loop conformations, which are different from those being in double-cone conformations in Pr₁₀ cluster.

In recent years, Dalgarno and co-workers have communicated four interesting examples of calixarene-based manganese clusters by the introduction of co-ligands. Specifically speaking, combination of phosphinate and 2-(hydroxymethyl)pyridine co-ligands results in the formation of unusual [Mn^{III}Mn^{II}]₂ dimer of dimers [17] and ferromagnetic [Mn^{III}₃Mn^{II}]₂ cages [18] supported by calix[4]arenes, respectively. Very recently, they have obtained a calix[4]arene-based [Mn^{III}Mn^{IV}] cluster by employing 3,5-dichlorobenzoate as co-ligand [19]. Moreover, by using phenyl salicylaldehyde as co-ligand, a novel [Mn^{III}Mn^{IV}] dimer based on the larger membered calix[8]arene has also been prepared

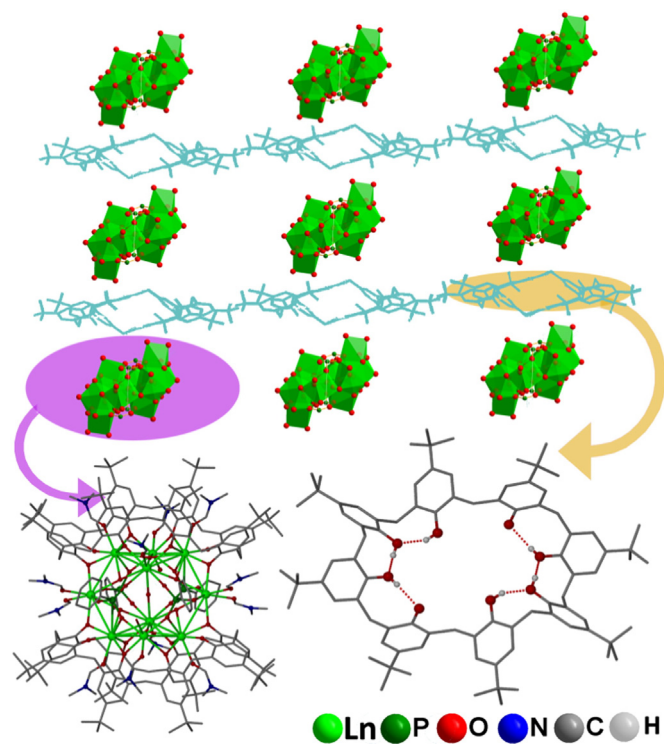


Fig. 3. Packing of the extended structure of compound **1** showing that the isolated Pr₁₀ cluster layers are separated by the layer of cocrystal H₆TBC8A²⁻ ligands (view along *b* axis). The dashed lines represent hydrogen bonds and other hydrogen atoms and isolated solvent molecules are omitted for clarity.

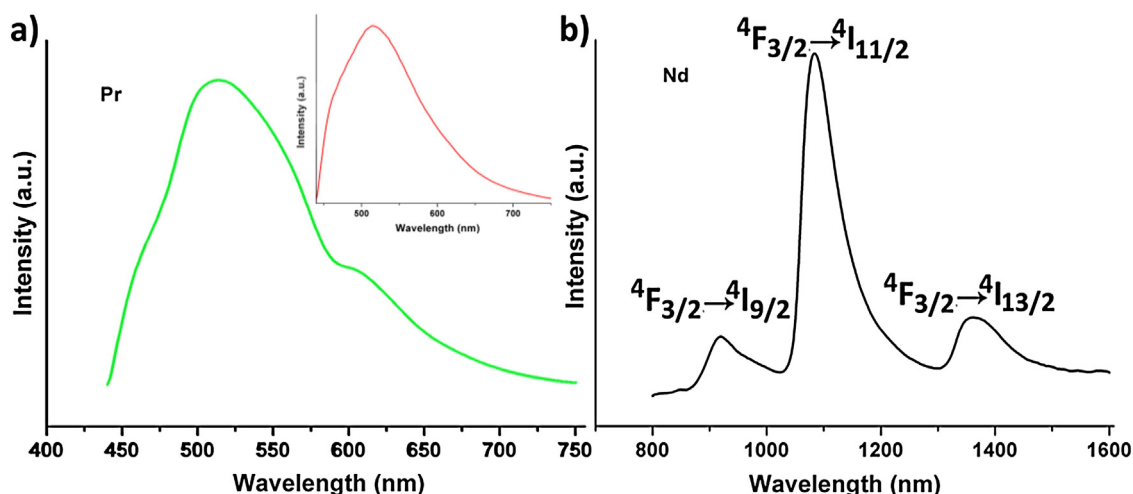


Fig. 4. The RT emission spectra for solid compounds **1** (a) and **2** (b) excited at 412 nm. Inset: Emission spectra of the free H_6TBC8A ligand excited at 330 nm in the solid state at room temperature.

[20]. However, there is no example of calixarene-based Ln clusters through the strategy of introducing co-ligands.

The solid-state emission spectra of compounds **1** and **2** at room temperature are depicted in Fig. 4. When excited at 412 nm, compound **1** shows a broad emission band at visible region centered at 512 nm (Fig. 4a). This kind of emission can be ascribed to the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electron transitions of coordinated ligand. Compound **2** exhibits the characteristic emissions of Nd^{3+} ion at the near-infrared region (Fig. 4b): 913, 1079, and 1351 nm, which are attributed to the $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, and $^4F_{3/2} \rightarrow ^4I_{13/2}$ transitions of Nd^{3+} ion, respectively [21].

The temperature dependence of magnetic susceptibilities is investigated on the polycrystalline sample of title compounds from 2 K to 300 K with an applied direct-current field of 1000 Oe (Fig. 5). The observed values of $\chi_m T$ at 300 K are 15.21 and 16.04 $cm^3 K mol^{-1}$ for **1** and **2**, respectively, which are close to the theoretical values of 16.00 and 16.40 $cm^3 K mol^{-1}$ for ten Pr^{III} (3H_4 , $S = 1$, $L = 5$, $g = 4/5$) and Nd^{III} ($^4I_{9/2}$, $S = 3/2$, $L = 6$, $g = 8/11$) in the free-ion approximation [22], respectively. Upon the temperature cooling, the $\chi_m T$ curves decrease continuously until reaching 1.40 and 10.24 $cm^3 K mol^{-1}$ for **1** and **2** at 2 K, respectively. The decrease of $\chi_m T$ for **1** is more rapidly than that of **2** in the low temperature region. For both compounds, the χ_m^{-1} vs. T data in the temperature range 50–300 K can be fitted by

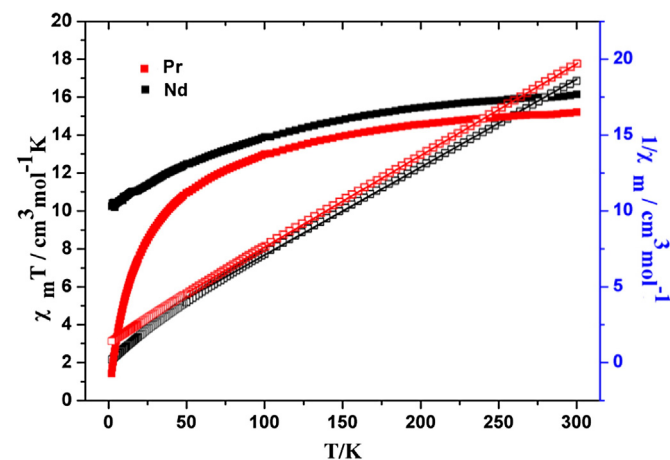


Fig. 5. The temperature dependence of magnetic susceptibility of **1** and **2** in a 1000 Oe field. The solid red and black lines are the fit of the experimental data of **1** and **2** using the Curie–Weiss law, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Curie–Weiss law to give $C = 16.56 cm^3 K mol^{-1}$ and $\theta = -27.27 K$ for **1**, and $C = 17.37 cm^3 K mol^{-1}$ and $\theta = -23.45 K$ for **2**. The negative θ values together with the decrease of the $\chi_m T$ curves upon cooling may be due to either antiferromagnetic interactions between spin centers or depopulation of the Stark sublevels of the Pr^{III} and Nd^{III} ions.

In conclusion, by employing phosphonate as co-ligand, we have obtained two new Ln_{10} clusters ($Ln = Pr, Nd$) with unusual self-assembly phenomenon that the cationic Ln_{10} cluster layers are separated by the layers of cocrystal H_6TBC8A^{2-} ligands. As far as we know, these two clusters represent the largest pure lanthanide clusters supported by H_6TBC8A ligands. The photoluminescent analyses show that compound **1** shows a broad emission band at visible region, while compound **2** exhibits the characteristic emissions of Nd^{3+} ion at the near-infrared region. The magnetic properties of both compounds were also examined, indicating strong antiferromagnetic interactions between the $Ln(III)$ centers and/or depopulation of the Stark sublevels of the $Ln(III)$ ions. Further work on using other calixarene or phosphonate ligands in the synthesis of high-nuclearity lanthanide coordination complexes with interesting structures and physicochemical attributes is underway.

Acknowledgments

This work was financially supported by the 973 Program (2011CB932504), Special Project of National Major Scientific Equipment Development of China (2012YQ120060), National Natural Foundation of China (21390392) and Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah (1-130-1434-HiCi).

Appendix A. Supplementary material

CCDC-1004493 and -1004494 contain the supplementary crystallographic data for compounds **1** and **2** in this paper. These data can be obtained free for charge via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2015.01.035>.

References

- [1] (a) F.-S. Guo, Y.-C. Chen, L.-L. Mao, W.-Q. Lin, J.-D. Leng, R. Tarasenko, M. Orendáč, J. Prokleškaet, Anion-templated assembly and magnetocaloric properties of a nanoscale $\{Gd_{38}\}$ Cage versus a $\{Gd_{48}\}$ barrel, *Chem. Eur. J.* 19 (2013) 14876–14885; (b) X.J. Kong, Y.L. Wu, L.S. Long, L.S. Zheng, Z.P. Zheng, A chiral 60-metal sodalite cage featuring 24 vertex-sharing $[Er_4(\mu_3-OH)_4]$ cubanes, *J. Am. Chem. Soc.* 131 (2009) 6918–6919.

- [2] M. Romanelli, G.A. Kumar, T.J. Emge, R.E. Riman, J.G. Brennan, Intense near-IR emission from nanoscale lanthanoid fluoride clusters, *Angew. Chem. Int. Ed.* 47 (2008) 6049–6051.
- [3] Y.L. Wang, Y. Ma, X. Yang, J. Tang, P. Cheng, Q.L. Wang, L.C. Li, D.Z. Liao, Syntheses, structures, and magnetic and luminescence properties of a new Dy(III)-based single-ion magnet, *Inorg. Chem.* 52 (2013) 7380–7386.
- [4] F.T. Edelmann, Lanthanide amidinates and guanidinates: from laboratory curiosities to efficient homogeneous catalysts and precursors for rare-earth oxide thin films, *Chem. Soc. Rev.* 38 (2009) 2253–2268.
- [5] (a) W.-H. Fang, G.-Y. Yang, Constructing heterometallic frameworks with highly connected topology based on edge-to-edge hexanuclear lanthanide clusters, *CrystEngComm* 16 (2014) 1885–1892;
(b) Z.-B. Han, G.-X. Zhang, M.-H. Zeng, D.-Q. Yuan, Q.-R. Fang, J.-R. Li, J. Ribas, H.-C. Zhou, Unprecedented marriage of a cationic pentanuclear cluster and a 2D polymeric anionic layer based on a flexible tripodal ligand and a Cu(II) ion, *Inorg. Chem.* 49 (2010) 769–771.
- [6] (a) R. Kumar, Y.O. Lee, V. Bhalla, M. Kumar, J.S. Kim, Recent developments of thiacalixarene based molecular motifs, *Chem. Soc. Rev.* 43 (2014) 4824–4870;
(b) Y.F. Bi, S.C. Du, W.P. Liao, Thiacalixarene-based nanoscale polyhedral coordination cages, *Coord. Chem. Rev.* 276 (2014) 61–72.
- [7] (a) F.R. Dai, U. Sambasivam, A.J. Hammerstrom, Z. Wang, Synthetic supercontainers exhibit distinct solution versus solid state guest-binding behavior, *J. Am. Chem. Soc.* 136 (2014) 7480–7491;
(b) M. Liu, S. Du, Y. Bi, W. Liao, A tetrahedral coordination cage based on p-tert-butylthiacalix[4]arene and 5-sulfoisophthalic acid, *Inorg. Chem. Commun.* 41 (2014) 96–99.
- [8] (a) S.M.T., Ruairaidh D. McIntosh, Sergio Sanz, Christine M. Beavers, Simon J. Teat, Euan K. Brechin, Scott J. Dalgarno, p-tert-Butylcalix[8]arene: a support for sodium and sodium-manganese clusters that exhibit interesting self-assembly properties, *Dalton Trans.* 40 (2011) 12265–12270;
(b) S. Du, Y. Bi, Y. Yu, W. Liao, Syntheses, structures and magnetic properties of $\text{Ln}^{\text{III}}\text{6Co}^{\text{II}}\text{8}$ (Ln = Sm, Gd, Dy) clusters capped by p-tert-butylcalix 8 arenes, *Sci. Sin. Chim.* 42 (2012) 1356–1363;
(c) S. Du, H. Ke, Y. Bi, H. Tan, Y. Yu, J. Tang, W. Liao, A Mn-5(II) tetragonal pyramid stabilized by p-tert-butylcalix 8 arene: Synthesis, structure and magnetic property, *Inorg. Chem. Commun.* 29 (2013) 85–88;
(d) R.D. Bergougnant, A.Y. Robin, K.M. Fromm, From simple rings to one-dimensional channels with calix 8 arenes, water clusters, and alkali metal ions, *Tetrahedron* (63) (2007) 10751–10757.
- [9] Y.-Z. Zheng, M. Evangelisti, F. Tuna, R.E.P. Winpenny, Co–Ln mixed-metal phosphonate grids and cages as molecular magnetic refrigerants, *J. Am. Chem. Soc.* 134 (2012) 1057–1065;
(b) S. Natarajan, S. Mandal, Open-framework structures of transition-metal compounds, *Angew. Chem. Int. Ed.* 47 (2008) 4798–4828.
- [10] K. Su, F. Jiang, J. Qian, Y. Gai, M. Wu, S.M. Bawaked, M. Mokhtar, S.A. Al-Thabaiti, M. Hong, Generalized synthesis of calixarene-based high-nuclearity M_{4n} nanocages (M = Ni or Co; n = 2–6), *Cryst. Growth Des.* 14 (2014) 3116–3123.
- [11] Su Kongzhao, Feilong Jiang, Jinjie Qian, Kang Zhou, Jiandong Pang, Sulaiman Basahel, Mihamed Mokhtar, Shaeel A. Al-Thabaiti, M. Hong, Calix[4]arene-based clusters with μ_9 -carbonato-bridged $\text{Co}^{\text{II}}\text{9}$ cores, *Inorg. Lett.* 1 (2014) 1–8.
- [12] K. Su, F. Jiang, J. Qian, J. Pang, S.A. Al-Thabaiti, S.M. Bawaked, M. Mokhtar, Q. Chen, M. Hong, Alkali-metal-templated assembly of two high-nuclearity cobalt clusters based on thiacalix[4]arene, *Cryst. Growth Des.* 14 (2014) 5865–5870.
- [13] (a) J.C.G. Bunzli, P. Froidevaux, J.M. Harrowfield, Photophysical properties of lanthanide dinuclear complexes with p-tert-butylcalix[8]arene, *Inorg. Chem.* 32 (1993) 3306–3311;
(b) S.M. Taylor, S. Sanz, R.D. McIntosh, C.M. Beavers, S.J. Teat, E.K. Brechin, S.J. Dalgarno, p-tert-Butylcalix[8]arene, an extremely versatile platform for cluster formation, *Chem. Eur. J.* 18 (2012) 16014–16022.
- [14] (a) H. Ke, G.F. Xu, L. Zhao, J. Tang, X.Y. Zhang, H.J. Zhang, A Dy_{10} cluster incorporates two sets of vertex-sharing Dy_3 triangles, *Chem. Eur. J.* 15 (2009) 10335–10338;
(b) X. Yang, R.A. Jones, M.J. Wiester, A nanoscale slipped sandwich of Tb_{10} -stabilization of a benzaldehyde methyl hemiacetyl, *Dalton Trans.* (2004) 1787–1788.
- [15] K. Xiong, F. Jiang, Y. Gai, Y. Zhou, D. Yuan, K. Su, X. Wang, M. Hong, A series of octanuclear-nickel(II) complexes supported by thiacalix[4]arenes, *Inorg. Chem.* 51 (2012) 3283–3288.
- [16] R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E. Winpenny, Interligand reactions: in situ formation of new polydentate ligands, *J. Chem. Soc. Dalton Trans.* (2000) 2349–2356.
- [17] S.M. Taylor, R.D. McIntosh, C.M. Beavers, S.J. Teat, S. Piligkos, S.J. Dalgarno, E.K. Brechin, Calix 4 arene supported clusters: a dimer of $\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}$ dimers, *Chem. Commun.* 47 (2011) 1440–1442.
- [18] S.M. Taylor, R.D. McIntosh, S. Piligkos, S.J. Dalgarno, E.K. Brechin, Calixarene-supported clusters: employment of complementary cluster ligands for the construction of a ferromagnetic $[\text{Mn}_5]$ cage, *Chem. Commun.* 48 (2012) 11190–11192.
- [19] R. McLellan, S.M. Taylor, R.D. McIntosh, E.K. Brechin, S.J. Dalgarno, Complementary ligands direct the formation of a calix[8]arene-supported ferromagnetic $\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}$ dimer, *Dalton Trans.* 42 (2013) 6697–6700.
- [20] S.M. Taylor, J.M. Frost, R. McLellan, R.D. McIntosh, E.K. Brechin, S.J. Dalgarno, Assembly of a calix[4]arene-supported $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}$ cluster mediated by halogen interactions, *CrystEngComm* 16 (2014) 8098–8101.
- [21] X. Yang, D. Schipper, R.A. Jones, L.A. Lytwak, B.J. Holliday, S. Huang, Anion-dependent self-assembly of near-infrared luminescent 24- and 32-metal Cd–Ln complexes with drum-like architectures, *J. Am. Chem. Soc.* 135 (2013) 8468–8471.
- [22] X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, G. Nichol, R.-B. Huang, L.-S. Zheng, Dual shell-like magnetic clusters containing Ni^{II} and Ln^{III} (Ln = La, Pr, and Nd) ions, *Inorg. Chem.* 47 (2008) 2728–2739.