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Framework Solids Possessing Both Hydrophobic and Hydrophilic Pores Constructed by Face-Sharing Keplerate-Type Heterometal–Organic Polyhedra

Xiang-Jian Kong,[a] Han Zhang,[a] Hai-Xia Zhao,[a] Yan-Ping Ren,*[a] La-Sheng Long,*[a] Zhiping Zheng,*[a, b] Gary S. Nichol,[b] Rong-Bin Huang,[a] and Lan-Sun Zheng[a]

The exploratory synthesis and investigation of properties of metal–organic framework (MOF) solids have received much interest in the last two decades,[1–6] driven largely by their useful applications in catalysis,[2] separations,[3] sensors,[4] electronics,[5] and gas storage.[6] Over the course of these investigations, the use of simple metal complexes and clusters as structural and functional building blocks have been extensively studied.

A more recent development in MOF construction makes use of metal–organic polyhedra (MOPs) as building units, prompted by their significantly larger size and high symmetry, traits that are propitious for making functional MOFs due to the enhanced control over the topology and size of the porous structures and the flexibility of incorporating desired functionalities.[7–10] A large number of MOFs featuring MOPs as supermolecular building blocks have in fact appeared in the literature.[11–12] Notwithstanding such progress, framework materials composed of heterometal MOPs are rare, particularly those that contain lanthanide elements, although such materials are probably more desirable for the realization of multifunctional materials with the possibility of facile property tailoring and performance optimization. On the other hand, research into 3d–4f compounds has mainly focused on the synthesis and magnetic studies of nonpolyhedral complexes;[13–14] obtaining 3d–4f MOPs has been a challenge due largely to the difficulty in simultaneously satisfying the distinctly different coordination requirements of transition and lanthanide elements.

We have, nevertheless, obtained a fascinating double-sphere Keplerate structure[15] that features an outer icosidodecahedron of 30 Ni^{II} ions that encapsulates an inner dodecahedron of 20 La^{III} ions.[16] Shortly thereafter, a giant Russian doll-like cluster composed of four cube-shape metallic shells was also achieved.[17] In both cases, the metallopolygons are encapsulated by iminodiacetate ligands that form mononuclear complex units with the Ni^{II} ions. While pursuing these novel heterometal MOPs, we have come to realize that the products are sensitively dependent on the reaction conditions, including the metal/ligand ratio, pressure, and the nature of the lanthanides.[18] More recently, while investigating how similar ligands may influence the reaction outcome, we obtained two novel porous framework solids that are constructed by face-sharing Keplerate-type 3d–4f MOPs,[19] as opposed to the discrete clusters previously reported.[16,17] The products, formulated as $\{[Ln_{12}Ni_{12}(DCTA)_{12}(H_2O)_x]\cdot[Ni(H_2O)_6]_3\cdot(ClO_4)_{18}\cdot(H_2O)_y\}_n$ (**1**: Ln = La, $x=60$, $y=30$; **2**: Ln = Gd, $x=24$, $y=80$; H_4DCTA = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetic acid) based on crystallographic studies and supported by satisfactory elemental analysis, were obtained by concentrating aqueous solutions that contained $Ni(NO_3)_2\cdot 6H_2O$, H_4DCTA, $Ln(ClO_4)_3$ (Ln = La (**1**), Gd (**2**)), and NaOH.

Crystallographic analysis revealed a complex yet regular framework structure with two distinct types of pores (Figure 1) for the two isostructural compounds, which differ only in the number of aqua ligands and water molecules of crystallization. Thus, only the structure of compound **1** is discussed below to illustrate the common salient structural features. The basic building unit is a heterometal–organic cage composed of 24 La atoms and 12 units of metalloligand

[a] X.-J. Kong, H. Zhang, H.-X. Zhao, Y.-P. Ren, L.-S. Long, Z. Zheng, R.-B. Huang, L.-S. Zheng
State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry
College of Chemistry and Chemical Engineering
Xiamen University, Xiamen 361005 (China)
Fax: (+86)592-218-3047
E-mail: ypren@xmu.edu.cn
lslong@xmu.edu.cn
zhiping@u.arizona.edu

[b] Z. Zheng, G. S. Nichol
Department of Chemistry and Biochemistry
University of Arizona
Tucson, Arizona 85721 (USA)

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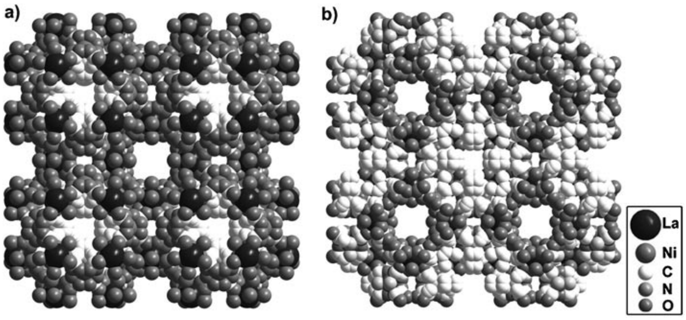

Figure 1. The space-filling plots of the hydrophobic and hydrophilic channels and the connecting motifs in between. The trapped guest species, ClO_4^- and $[Ni(H_2O)_6]^{2+}$ ions, are omitted for clarity.

$[Ni(DCTA)]^{2-}$ (Figure 2) with the $(DCTA)^{4-}$ carboxylate groups bridging the two different types of metal atoms. Connecting the La atoms generates a perfect rhombicuboctahedron (Figure 3a), an Archimedean polyhedron with eight triangular and eighteen square faces. Six of the squares are characterized by the fact that they only share vertices with the triangles. It is by sharing these unique faces of the heterometal–organic rhombicuboctahedra that the overall framework structure of **1** is achieved. Each of the remaining and unshared twelve square faces is capped by a $[Ni(DCTA)]^{2-}$ moiety. Linking the Ni atoms generates a cuboctahedron (Figure 3a), a different Archimedean polyhedron with 24 identical edges, in the middle of each of which resides a La atom. This double-MOP structure featuring an outer rhombicuboctahedron encapsulating an inner cuboctahedron represents a rare example of two nesting Archimedean polyhedra.[20–22] The outer La_{24} cage has a diameter of 21.0 Å, whereas the inner cage of Ni_{12} has an interior dimension of 13.7 Å. Within the individual cages, the separations between neighboring metal atoms are 8.7352(6) and 8.6873(5) Å (La···La) and 9.6850(11) Å (Ni···Ni).

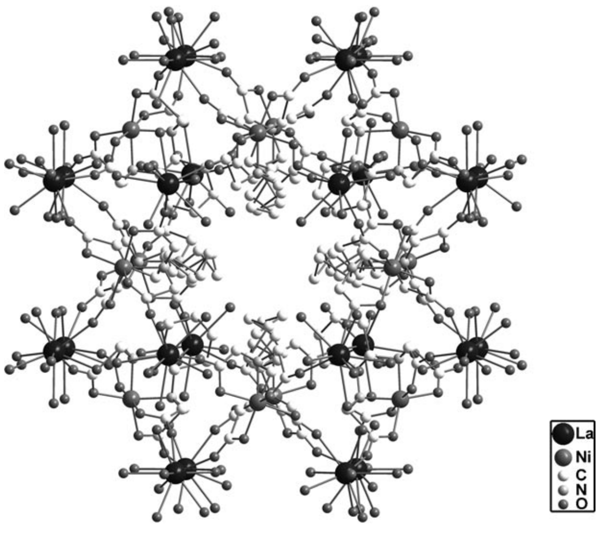

Figure 2. The structure of $La_{24}[Ni(DCTA)]_{12}$, the polyhedral heterometal–organic building unit of **1**.

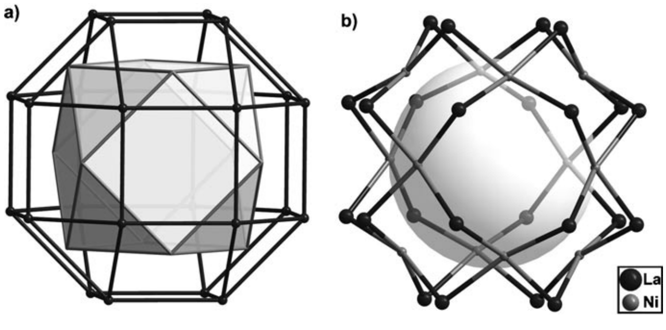

Figure 3. a) The outer rhombicuboctahedron of La_{24} encapsulates the inner cuboctahedron of Ni_{12}. b) The $La_{24}Ni_{12}$ cage can be viewed as constructed by eight chair-like units of La_3Ni_3 or six crown-like units of La_4Ni_4.

Connecting neighboring metal atoms in these two cages results in an aesthetically pleasing 36-metal (24 La and 12 Ni) assembly (Figure 3b). It may be viewed as a construct of eight chair-like La_3Ni_3 hexagonal units by sharing the Ni vertices or of six crown-like La_4Ni_4 units by sharing the four Ni atoms along its bottom edge. The separation between the nearest La and Ni atoms is 6.2073(1) Å.

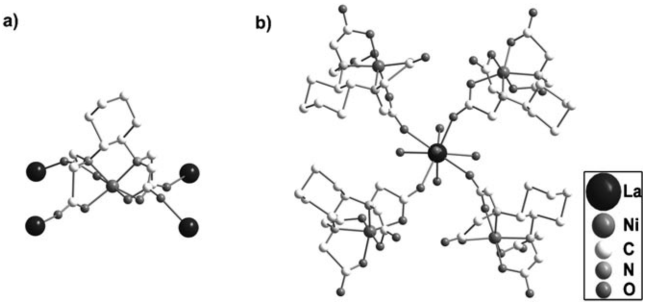

Figure 4. a) The structure of the metalloligand $[Ni(DCTA)]^{2-}$ and b) the coordination sphere of an La^{3+} ion.

A further analysis of the crystal structure reveals that the $(DCTA)^{4-}$ ligand utilizes its two N atoms and four O atoms, one from each of the carboxylate groups, for Ni coordination; the other carboxylato O atoms are left for La coordination, which renders $[Ni(DCTA)]^{2-}$ a tetratopic metalloligand (Figure 4a). On the other hand, each La atom is nonacoordinate with five aqua ligands and four $[Ni(DCTA)]^{2-}$ metalloligands; each of the latter contributes only one carboxylato O atom (Figure 4b). In fact, the compounds are prepared modularly by first forming the $[Ni(DCTA)]^{2-}$ metalloligand,[23] followed by coordination with a lanthanide ion. The ability to obtain isomorphous complexes with different lanthanide ions suggests that the present molecular design is rational and reliable. Furthermore, an interesting view of the framework arises due to these two unique building blocks: The same structure can alternatively be viewed as being built by the face-sharing $[Ni(DCTA)]_{24}La_{12}$, a heterometal–organic rhombicuboctahedron that is structurally equivalent to the aforementioned

$La_{24}[Ni(DCTA)]_{12}$. In such a scenario, the 24 vertices of the rhombicuboctahedron are the metalloligands and each of its twelve unique square faces is capped by a La atom (Figure 5a). Correspondingly, these La atoms form a cuboctahedron. The Ni_{24} cage possesses a nanoscopic interior of 21.0 Å, whereas the inner cuboctahedron of 12 La atoms has a diameter of 12.3 Å (Figure 5b). The separations between neighboring metal atoms are 7.3441(16) and 9.6850(11) Å (Ni···Ni) and 8.7352(6) Å (La···La).

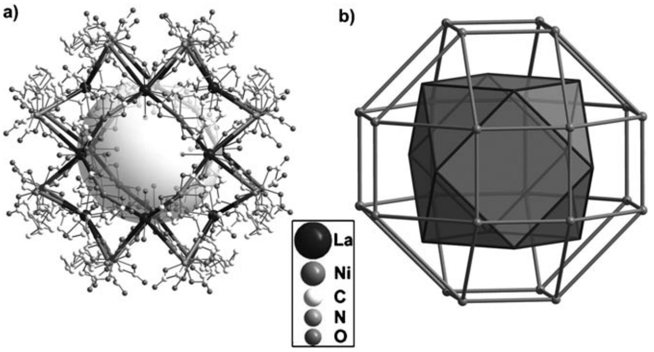

Figure 5. a) The structure of the heterometal–organic cage $[Ni(DCTA)]_{24}La_{12}$ and b) the outer rhombicuboctahedron of Ni_{24} that encapsulates the inner cuboctahedron of La_{12}.

The 3D framework is constructed by using the heterometal–organic rhombicuboctahedra $La_{24}[Ni(DCTA)]_{12}$ or $[Ni(DCTA)]_{24}La_{12}$ as the secondary building unit through sharing of their quadrangle faces. Because of the equivalency of these two building blocks, the framework structure may be viewed as interpenetrating cubic arrays of the La_{24} and Ni_{24} cages (Figure 6). Each La_{24} cage is situated in an octahedral interstitial site formed by six identical La_{24} cages (Figure 7a). When placed with respect to the framework composed of Ni_{24} cages, each La_{24} cage is located in a cubic interstitial site formed by eight Ni_{24} cages (Figure 7b), which forms a CsCl-type structure.

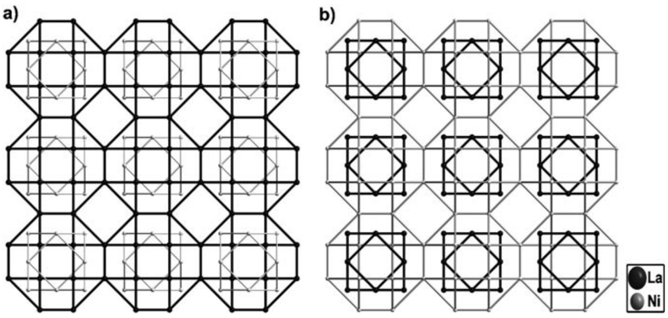

Figure 6. Packing view of a) the $Ni_{12}@La_{24}$ array and b) the $La_{12}@Ni_{24}$ array.

Notably, there are two types of pores in the structure with distinctly different interior environments, one hydrophobic and the other hydrophilic. The former can be clearly identified when one looks at the interior of the $La_{24}[Ni(DCTA)]_{12}$ cage, whereas the latter is the central void present in the cube formed by eight such face-sharing rhombicuboctahedra (Figure 1a). Analogously, the hydrophilic pores can be readily discerned by building the framework with the equivalent $[Ni(DCTA)]_{24}La_{12}$ units; forming a cube using eight of such rhombicuboctahedra leaves a body-centered hydrophobic pore (Figure 1b). A view through the cell body diagonal of $La_{24}[Ni(DCTA)]_{12}$ and $[Ni(DCTA)]_{24}La_{12}$ reveals two hexagon-shaped rings (Figure 8a and b) that were found at 24.4 and 23.5 Å, respectively, between the opposite vertices (M···M distances); the $(DCTA)^{4-}$ cyclohexanyl rings are positioned in the interior of the $La_{24}[Ni(DCTA)]_{12}$ cage, rendering it hydrophobic, whereas the interior of the structurally equivalent $[Ni(DCTA)]_{24}La_{12}$ cage is decorated with La-bound aqua ligands with the organic moieties pointing away from it, and is thus hydrophilic. Occupying the hydrophobic pores are ClO_4^- ions, whereas $[Ni(H_2O)_6]^{2+}$ ions are found trapped in the hydrophilic pores and the areas at which the face-sharing occurs.

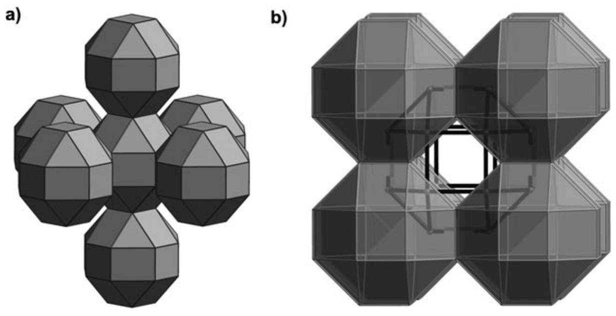

Figure 7. a) View of the individual La_{24} cages within the cubic array formed by these nanoscopic building blocks and b) the CsCl-type structure constructed from interpenetrating cubic arrays of La_{24} and Ni_{24} cages viewed along the [100] direction.

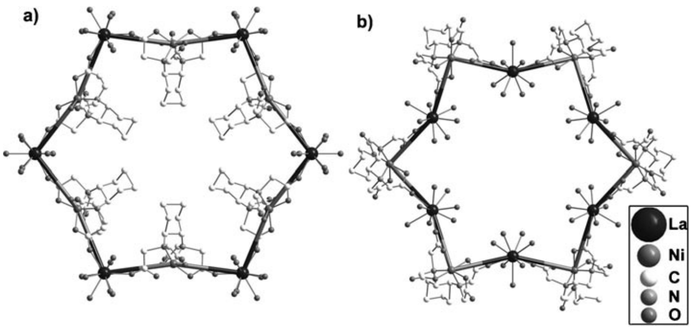

Figure 8. a) The $La_6Ni_6(DCTA)_6$ unit in $La_{24}[Ni(DCTA)]_{12}$ viewed along the cell body diagonal [111] direction and b) the $La_6Ni_6(DCTA)_6$ unit in $[Ni(DCTA)]_{24}La_{12}$ viewed along the cell body diagonal [111] direction.

Thermogravimetric analyses (Figure S1 in the Supporting Information) of **1** and **2** gave essentially the same results. For compound **1**, an initial weight loss of 18.1% between room temperature and 200 °C suggests the loss of water molecules of crystallization and the aqua ligands (calcd 18.7 %). No further weight loss was observed between 200 and 350 °C, which indicates that the composition of the dehydrated product remains unchanged over this temperature range. Variable-temperature X-ray powder diffraction (XRD) patterns were obtained to identify any structural transitions that accompany the temperature change (Figure S2 in the Supporting Information). Upon heating from 30 to 80 °C, the number of diffraction peaks decreases dramatically with peak broadening. Further temperature increases to 120 and then 250 °C caused complete disappearance of the remaining peaks. Intriguingly, cooling of this sample to 30 °C followed by exposure to air for 48 h gave the same XRD patterns as produced by the as-synthesized sample, which suggests that the framework structure survived the dehydration process and that the original structure can be restored. The featureless XRD pattern may reflect possible severe crystallographic disorder associated with the necessary reorganization of the inherently flexible coordination sphere of the La^{3+} ions upon removal of the aqua ligands.

The dehydrated sample was then exposed to dry methanol and tetrahydrofuran. The XRD patterns in both cases remained essentially featureless (Figure S4 and S5 in the Supporting Information), which suggests that these solvent molecules were not taken into the porous structure, and is probably a reflection of the enhanced steric hindrance with respect to a water molecule.

The magnetic susceptibilities of **1** and **2** were measured in an applied field of 1000 Oe over the temperature range of 2 to 300 K and are shown as plots of $\chi_M T$ (Figure 9) and χ_M^{-1} (Figure S5 and S6 in the Supporting Information) versus T. For compound **1**, the $\chi_M T$ value of 14.88 $cm^3 K mol^{-1}$ at 300 K is close to the value of 15.00 $cm^3 K mol^{-1}$ calculated for 15 uncorrelated Ni^{II} ions ($S=1$, $g=2.00$). This value remains essentially constant between 20 and 300 K, indicating the paramagnetic nature of this compound in this temperature range. Upon lowering of the temperature, the $\chi_M T$ drops to 6.11 $cm^3 K mol^{-1}$ at 2 K, which suggests very weak antiferromagnetic coupling Ni^{II} centers within the molecule, but possibly combined with the effect of zero-field splitting of the Ni^{II} ground-state terms.[24]

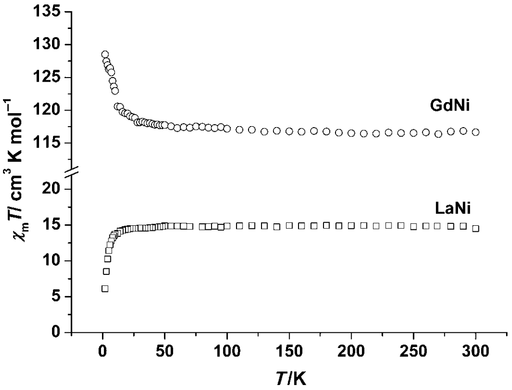

Figure 9. Plots of $\chi_M T$ vs. T for compounds **1** (bottom) and **2** (top).

For compound **2**, the $\chi_M T$ value of 116.66 $cm^3 K mol^{-1}$ at 300 K is slightly larger than the value of 109.56 $cm^3 K mol^{-1}$ calculated for 15 uncorrelated Ni^{II} ions (15.00 $cm^3 K mol^{-1}$, $S=1$, and $g=2.00$) and 12 uncorrelated Gd^{III} ions in the $^8S_{7/2}$ ground state (94.56 $cm^3 K mol^{-1}$, $g=2.00$). Over the temperature range of 30 to 300 K, $\chi_M T$ remains essentially constant. Upon further lowering of the temperature, $\chi_M T$ increases rapidly and reaches a value of 128.51 $cm^3 K mol^{-1}$ at 2 K, which suggests ferromagnetic interactions between the Ni^{II} and Gd^{III} ions. The temperature dependence of the molar susceptibility between 300 and 2 K is described well by a Curie–Weiss law, $\chi = C/(T\text{-}\Theta)$, in which $C=$ 116.4 $cm^3 K mol^{-1}$ and $\Theta = 0.49$ K, consistent with weak ferromagnetic coupling between the Ni^{II} and Gd^{III} ions. This interaction is emphasized by the temperature dependence of the difference in $\chi_M T$ between the two compounds, $\Delta = (\chi_M T)(\mathbf{2}) - (\chi_M T)(\mathbf{1})$, as shown in Figure S7 in the Supporting Information. The rapid increase in Δ as T approaches 2 K can be ascribed to Gd–Ni ferromagnetic interactions, assuming that the Gd–Gd coupling is negligibly small due to the confinement of the f electrons.

In summary, two novel framework structures based on unprecedented 3d–4f heterometal–organic polyhedra have been reported. The polyhedral building unit possesses a Keplerate-type double-Archimedean solid structure that features an outer rhombicuboctahedron encapsulating an inner cuboctahedron. Face-sharing of these units leads to frameworks with both hydrophilic and hydrophobic pores of nanoscopic dimensions. Thermal analysis coupled with variable-temperature XRD studies suggest that the framework integrity is maintained upon dehydration and that the original structure can be reinstated on rehydration, and that the overall structure is dynamic and exhibits both the "regularity" and "softness" characteristic of flexible metallo–organic framework structures.[26] Presently we are exploring the possibility of incorporating suitable ancillary ligands (e.g. pyridine) into the pores by carrying out the synthesis in the presence of such "guest species" to help the pore structure survive dehydration. Prompted by the drastically different magnetic properties exhibited by two isomorphous compounds that differ only in the nature of the lanthanide ions, we will also be focusing on the systematic synthesis and property tailoring of closely related analogues by using various combinations of metals and functionalized ligands. Efforts to create pore structures capable of recognizing and storing guest species based on chiral discrimination by using, for example, 1,2-diaminopropane-*N,N,N′,N′*-tetraacetic acid (a chiral analogue of DCTA), are also in progress.

Experimental Section

Synthesis of 1: An aqueous solution (10 mL) containing $Ni(NO_3)_2 \cdot 6H_2O$ (0.58 g, 2.0 mmol) and *trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid monohydrate ($H_4DCTA{\cdot}H_2O$; 0.728 g, 2.0 mmol) was stirred at 80 °C, and its pH was adjusted to 6 with the addition of aqueous NaOH (1.0 M). The resulting mixture was heated at reflux for 10 min, after which aqueous $La(ClO_4)_3$ (1.0 M, 2 mL) was added. The pH of the resulting mixture was readjusted to ≈6 with aqueous NaOH (1.0 M). After heating at reflux for 2 h, the reaction mixture was filtered to afford a deep blue solution from which crystals of the product were obtained upon standing under ambient conditions for two months (yield: 45.0 % based on $Ni(NO_3)_2$). Elemental analysis calcd (%) for $\{[La_{12}Ni_{12}(DCTA)_{12}(H_2O)_{60}]{\cdot}[Ni(H_2O)_6]_3{\cdot}(ClO_4)_{18}{\cdot}(H_2O)_{30}\}_n$ ($La_{12}Ni_{15}C_{168}N_{24}O_{276}H_{432}Cl_{18}$, $M_r = 10391.05$ based on 30 water molecules of crystallization): C 19.42, H 4.19, N 3.24; found: C 19.30, H 4.12, N 3.36.

Synthesis of 2: Compound **2** was prepared by using $Gd(ClO_4)_3$ in place of $La(ClO_4)_3$ under otherwise identical conditions as those described above for the synthesis of **1** (yield: 40.0 % based on $Ni(NO_3)_2$). Elemental analysis calcd (%) for $\{[Gd_{12}Ni_{12}(DCTA)_{12}(H_2O)_{24}]{\cdot}[Ni(H_2O)_6]_3{\cdot}(ClO_4)_{18}{\cdot}(H_2O)_{80}\}_n$ ($Gd_{12}Ni_{15}C_{168}N_{24}O_{290}H_{460}Cl_{18}$, $M_r = 10862.99$ based on 80 water molecules of crystallization): C 18.57, H 4.27, N 3.09; found: C 18.22, H 4.21, N 3.19.

Crystal data for **1** and **2** are given in the Supporting Information. CCDC-744657 (**1**) and -751621 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: cage compounds · heterometallic complexes · lanthanides · metal–organic frameworks · structure elucidation

[1] J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213–1214.

[2] C.-Y. Sun, S.-X. Liu, D.-D. Liang, K-Z. Shao, Y.-H. Ren, Z.-M. Su, *J. Am. Chem. Soc.* **2009**, *131*, 1883–1888.

[3] R. B. Custelcean, A. Moyer, *Eur. J. Inorg. Chem.* **2007**, 1321–1340.

[4] B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, *J. Am. Chem. Soc.* **2004**, *126*, 15394–15395.

[5] A. Harriman, R. Ziessel, *Coord. Chem. Rev.* **1998**, *171*, 331–339.

[6] S. S. Han, J. L. Mendoza-Cortés, W. A. Goddard III, *Chem. Soc. Rev.* **2009**, *38*, 1460–1467.

[7] a) J. J. Perry IV, A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417; b) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835; c) J. J. Perry IV, V. C. Kravtsov, G. J. McManus, M. J. Zaworotko, *J. Am. Chem. Soc.* **2007**, *129*, 10076–10077; d) D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2008**, *120*, 5214–5225; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136–5147.

[8] a) J.-R. Li, D. J. Timmons, H.-C. Zhou, *J. Am. Chem. Soc.* **2009**, *131*, 6368–6369; b) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2042; c) H. Chun, *J. Am. Chem. Soc.* **2008**, *130*, 800–801.

[9] a) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, Y. Wei, S. L. Qiu, R. R. Xu, *Angew. Chem.* **2005**, *117*, 3913–3916; *Angew. Chem. Int. Ed.* **2005**, *44*, 3845–3848; b) F. Nouar, J. Eckert, J. F. Eubank, P. Forster, M. Eddaoudi, *J. Am. Chem. Soc.* **2009**, *131*, 2864–2870.

[10] a) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; b) Y. Zou, M. Park, S. Hong, M. Lah, *Chem. Commun.* **2008**, 2340–2342.

[11] a) T. Wu, J. Zhang, C. Zhou, L. Wang, X. H. Bu, P. Y Feng, *J. Am. Chem. Soc.* **2009**, *131*, 6111–6113; b) K. H. Li, D. H. Olson, J. Seidel, T. J. Emge, H. W. Gong, H. P. Zeng, J. Li, *J. Am. Chem. Soc.* **2009**, *131*, 10368–10369.

[12] a) Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey, M. Schröder, *Chem. Commun.* **2009**, 1025–1027; b) A. Sonnauer, F. Hoffmann, M. Fröba, L. Kienle, V. Duppel, M. Thommes, C. Serre, G. Férey, N. Stock, *Angew. Chem.* **2009**, *120*, 3849–3852; *Angew. Chem. Int. Ed.* **2009**, *48*, 3791–3794.

[13] J.-W. Cheng, J. Zhang, S.-T. Zheng, M.-B. Zhang, G.-Y. Yang, *Angew. Chem.* **2006**, *118*, 79–83; *Angew. Chem. Int. Ed.* **2006**, *45*, 73–77.

[14] a) A. Mishra, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 15648–15649; b) S. C. Xiang, S. M. Hu, T. L. Sheng, R. B. Fu, X. T. Wu, X. D. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 15144–15146.

[15] a) A. Müller, *Science* **2003**, *300*, 749–750; b) A. Müller, *Nature* **2007**, *447*, 1035–1035; c) A. Müller, P. Kögerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218.

[16] X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, R.-B. Huang, L.-S. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 7016–7017.

[17] X. J. Kong, Y. P. Ren, W. X. Chen, L. S. Long, Z. P. Zheng, R. B. Huang, L. S. Zheng, *Angew. Chem.* **2008**, *120*, 2432–2435; *Angew. Chem. Int. Ed.* **2008**, *47*, 2398–2401.

[18] X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, T. D. Harris, Z. Zheng, *Chem. Commun.* **2009**, 4354–4356.

[19] The term MOP is generally reserved for discrete metal–organic polyhedrons that may exist separately and MOFs generally involve the use of bridging ligands (ref. [7a]). The present use of such terms is for the ease of description of structures in which MOP units, though not discrete, are clearly recognizable.

[20] S. Alvarez, *Datlon Trans.* **2005**, 2209–2233.

[21] M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem.* **2004**, *116*, 5739–5743; *Angew. Chem. Int. Ed.* **2004**, *43*, 5621–5625.

[22] N. T. Tran, D. R. Powell, L. F. Dahl, *Angew. Chem.* **2000**, *112*, 4287–4291; *Angew. Chem. Int. Ed.* **2000**, *39*, 4121–4125.

[23] Y.-X. Long, L.-S. Long, R.-B. Huang, L.-S. Zheng, S. W. Ng, *Acta Crystallogr. Sect. E* **2005**, *61*, m790–m792.

[24] Y. Yukawa, G. Aromí, S. Igarashi, J. Ribas, S. A. Zvyagin, J. Krzystek, *Angew. Chem.* **2005**, *117*, 2033–2037; *Angew. Chem. Int. Ed.* **2005**, *44*, 1997–2001.

[25] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

[26] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem. Biol.* **2009**, *1*, 695–704.

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