Magnetocaloric Effect

DOI: 10.1002/anie.201105147

A 48-Metal Cluster Exhibiting a Large Magnetocaloric Effect**

Jun-Bo Peng, Qian-Chong Zhang, Xiang-Jian Kong, Yan-Ping Ren, La-Sheng Long,* Rong-Bin Huang, Lan-Sun Zheng, and Zhiping Zheng*

Magnetic refrigeration, an energy-efficient and environmentally friendly technique operating on the basis of the magnetocaloric effect (MCE), has received much recent interest due to the possibility of replacing the expensive and increasingly rare helium-3 in ultralow-temperature ($\ll 1$ K) refrigeration. Although the MCE is an intrinsic property of a magnetic solid, only a few substances have been shown to display a sufficiently large MCE to be potentially useful.[1–4]

A molecule exhibiting a large MCE usually has a large-spin ground state, negligible magnetic anisotropy, low-lying excited spin states, dominant ferromagnetic exchange, and a large metal/ligand mass ratio.[1–6] In this regard, 3d Gd^{3+} heterometallic cluster complexes with small ligands are logical candidates. First, the isotropic electronic configuration of Gd^{3+} affords multiple low-lying excited spin states, while the disparate d^n/f^7 electronic configurations offer the possibility of a large-spin ground state as long as the nuclearity of the cluster is sufficiently high.[3,4] Second, a high-nuclearity cluster complex with small ligands naturally leads to a large metal/ligand mass ratio.[7] In constructing high-nuclearity 3d–4f cluster complexes, self-assembly of the metal ions has been remarkably successful.[8,9] Frequently, small anionic species are found in the cluster structures, and their presence can be readily appreciated in terms of their templating effects.[10]

We have now used acetate ligands to prepare a structurally fascinating 48-metal cluster complex, formulated as $[Gd_{36}Ni_{12}(CH_3COO)_{18}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}O)_6(H_2O)_{54}(NO_3)Cl_2](NO_3)_6Cl_9\cdot 30H_2O$ (**1**) on the basis of crystallographic studies and supported by satisfactory elemental analyses,[11] whereby the presence of Cl^- and NO_3^- in the cluster cation is believed to be critical for formation of the final product. Compound **1** shows impressively large entropy changes with changing field when compared with previously known 3d–4f cluster complexes.

Compound **1** was obtained from the reaction of $Gd(NO_3)_3$, $Ni(CH_3COO)_2$, and NaCl in ethanol/water. Single-crystal X-ray diffraction studies revealed a tubelike cationic cluster (Figure 1) consisting of 36 Gd^{3+}, 12 Ni^{2+}, 84 OH^-, 6 O^{2-}, 54 H_2O, and 18 acetate ligands, together with one NO_3^- and two Cl^- ions that are confined inside the tube. Such a tubular arrangement of metal ions is very rare in metal cluster compounds,[12] and in fact is the first such example in 3d–4f heterometallic clusters.

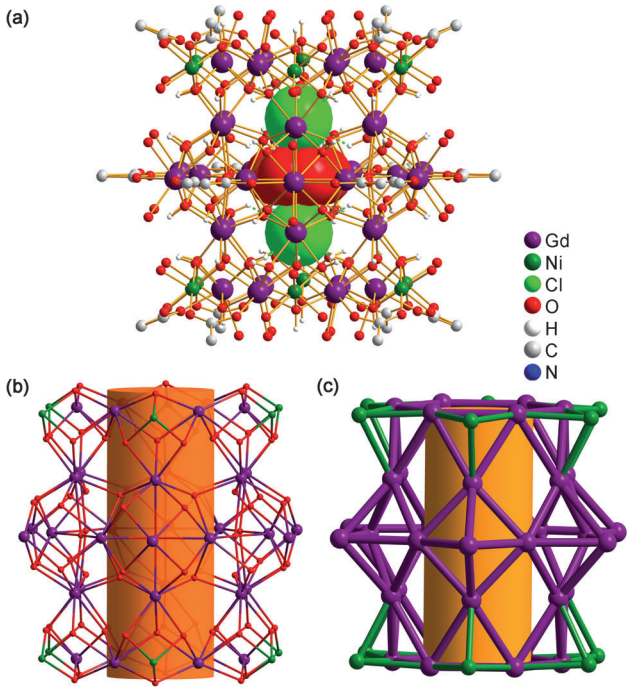

Figure 1. a) Ball-and-stick view of the cluster cation in **1** along the *c* axis. b) Structure of the $[Gd_{36}Ni_{12}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}O)_6]^{36+}$ cluster core in **1**. c) Arrangement of the 48 metal ions in **1**.

The structure of the $[Gd_{36}Ni_{12}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}O)_6]^{36+}$ cluster core can be viewed as a "sandwich" of two different kinds of cluster wheels (Figure 1b). The outer "bread" layer is wheel of six vertex-sharing $[Gd_3Ni(\mu_3\text{-}OH)_4]^{7+}$ units, and each of these cubane-like cluster units (Figure 2a) is connected to two identical neighbors by sharing two Gd atoms, producing an 18-metal $[Gd_{12}Ni_6(\mu_3\text{-}OH)_{24}]^{24+}$ hexagonal wheel (Figure 2c and e). A Cl^- ion is found in the center of the wheel, hydrogen-bonded to six μ_3-OH^- (four Cl···O 3.306(9) Å, Cl···H–O 166.76°; two Cl···O 3.324(12) Å, Cl···H–O 168.77°). Previously, a dodecanuclear lanthanide hydroxide cluster complex with two central templating iodide ions was reported.[13]

[*] J.-B. Peng,[+] Q.-C. Zhang,[+] Dr. X.-J. Kong, Dr. Y.-P. Ren, Prof. Dr. L.-S. Long, Prof. Dr. R.-B. Huang, Prof. Dr. L.-S. Zheng, Prof. Dr. Z. 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)
E-mail: xjkong@xmu.edu.cn
lslong@xmu.edu.cn

[+] These authors contributed equally to this work.

[**] We thank the NNSFC (Grants 20825103, 20901064, 90922031, 2007CB815304 and 21021061) and the Fundamental Research Funds for the Central Universities (No 2010121016) for support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105147.

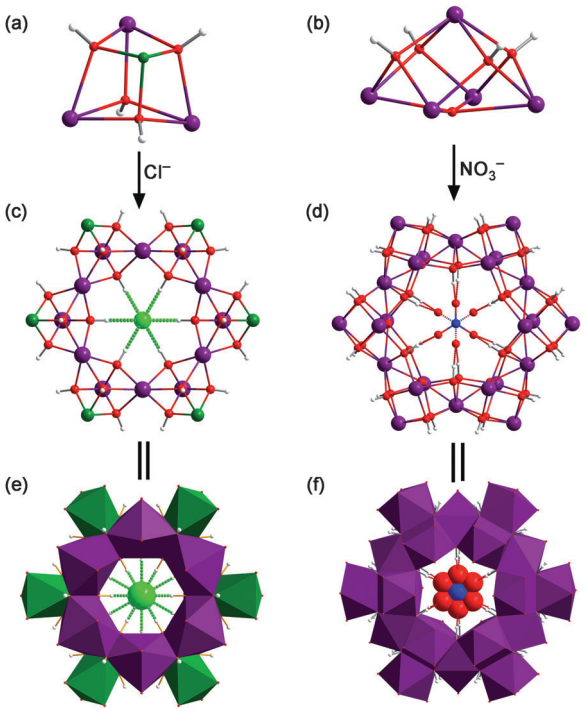

Figure 2. a) The cubane-like $[Gd_3Ni(\mu_3\text{-}OH)_4]^{7+}$ unit. b) The $[Gd_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$ unit. c) The approximately square-pyramidal $[Gd_{12}Ni_6(\mu_3\text{-}OH)_{24}Cl]^{23+}$ unit. d) The $[Gd_{24}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{36}(NO_3)]^{23+}$ unit. e) Polyhedral view of the $[Gd_{12}Ni_6(\mu_3\text{-}OH)_{24}Cl]^{23+}$ unit. f) Polyhedral view of the $[Gd_{24}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{36}(NO_3)]^{23+}$ unit.

The sandwiched cluster wheel is composed of six $[Gd_5(\mu_4\text{-}O)(\mu_3\text{-}OH)_4]^{9+}$ units joined together with two identical neighbors by sharing two basal Gd atoms of the roughly square-pyramidal cluster (Figure 2b) and two μ_3-OH^- groups, generating a hexagonal 24-metal assembly of $[Gd_{24}(\mu_4\text{-}O)_6(\mu_3\text{-}OH)_{36}]^{24+}$ (Figure 2d and f). This assembly is templated by a NO_3^- ion that is hydrogen-bonded to six μ_3-OH^- groups (four O···H–O 3.004(11) Å, O···H–O 155.68°; two O···H–O 3.001(12) Å, O···H–O 155.78°) along the inner rim of the wheel. NO_3^- ions acting as templates have been reported in 3d–4f metal clusters.[14]

The outer 18-metal cubane assemblies and the sandwiched 24-metal assembly of square-pyramidal clusters are connected by sharing six Gd atoms between adjacent wheels, producing the tubelike core of $[Gd_{36}Ni_{12}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}O)_6]^{36+}$ (Figure 1b). The 48 metal ions themselves are organized into 12 Gd_3Ni tetrahedrons and six Gd_5 square pyramids (Figure 1c). The cluster core is stabilized by 18 crystallographically disordered acetato and 54 terminal aqua ligands, in addition to the μ_3-OH^- and μ_4-O^{2-} ligands. The Gd···Ni and Gd···Gd distances of 3.414(2)–3.451(2) Å and 3.7002(7)–3.8681(9) Å, respectively, are comparable to the corresponding values in previously reported Gd–Ni clusters.[15]

The temperature dependence of the magnetic susceptibility of **1** was measured from 2 to 300 K in an applied magnetic field of 1000 Oe. The plot of $\chi_M T$ versus T is shown in Figure 3. The observed $\chi_M T$ value of 290.0 $cm^3 mol^{-1} K$ at 300 K is in good agreement with the value calculated for 12 uncorrelated Ni^{2+} ions (12 $cm^3 mol^{-1} K$ for $S=1$, $g=2.00$) and

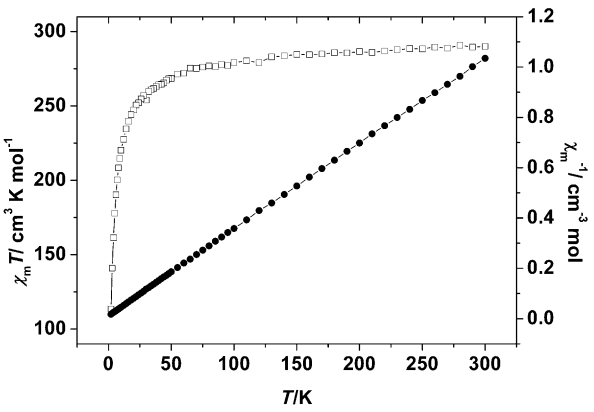

Figure 3. Plots of temperature dependence of $\chi_M T$ (□) and χ_M^{-1} (●) for **1** under 1000 Oe dc field between 2 and 300 K.

36 uncorrelated Gd^{3+} ions (283.68 $cm^3 K mol^{-1}$ for $S=7/2$, $g=2$). With decreasing temperature, the $\chi_M T$ value decreases gradually, and a value of 268.43 $cm^3 K mol^{-1}$ is reached at 50 K. On further lowering the temperature, $\chi_M T$ drops abruptly, and a value of 113.36 $cm^3 mol^{-1} K$ is reached at 2 K, which may be ascribed to a combination of the antiferromagnetic interaction and the zero-field splitting of the ground states.[3,4,15] The data in the range of 2–300 K can be fitted to the Curie–Weiss law, yielding $C=280.89$ $cm^3 K mol^{-1}$ and $\theta=-3.95$ K. Magnetization measurements in the 2–10 K temperature range were also performed (Figure 4a). The magnetization M of 225.69 $N\mu_B$ (where N is the Avogadro constant and μ_B is the Bohr magneton) at 2 K is smaller than expected if all spins of the metal ions were ferromagnetically aligned (319.7 $N\mu_B$).

The large magnetization values make **1** a possible candidate for low-temperature magnetic cooling, as magnetic entropy change ΔS_m, a key parameter in evaluating the MCE, can be calculated by applying the equation $\Delta S_m(T)=\int[\partial M(T,H)/\partial T]_H dH$ to the experimentally obtained magnetization data.[2–5] The entropy changes at various magnetic fields and temperatures are summarized in Figure 4b, with an impressive $-\Delta S_m=36.3$ $J kg^{-1} K^{-1}$ at 3 K for $\Delta H=7$ T. This value represents an increase of 45% over the highest literature value of 25.0 $J kg^{-1} K^{-1}$ calculated by the same method for an Mn_{14} cage,[1a] but lower than the value calculated from heat capacity by Evangelisti et al. (about 40 $J kg^{-1} K^{-1}$ at 1.8 K for $\Delta H=7$ T).[2] Assuming $S_{Ni}=1$ and $S_{Gd}=7/2$ at low temperature, the calculated $-\Delta S_m$ value per mole corresponding to 36 uncorrelated Gd^{3+} spin and 12 uncorrelated Ni^{2+} spins is 64.8 $J kg^{-1} K^{-1}$ based on $-\Delta S_m=nR\ln(2s+1)=36R\ln(8)+12R\ln(3)=88.0R$.[2,3a,4] The experimental value is smaller than the theoretical value, which is attributed to the presence of intracluster antiferromagnetic interactions and the Ni crystal-field effect. The large MCE observed may be attributable to the large metal/ligand mass ratio, and the use of small-molecule ligands such as acetate in the present work is helpful in achieving high spin density in high-nuclearity metal clusters.

In summary, a tubelike, 48-metal 3d–4f $Gd_{36}Ni_{12}$ cluster was synthesized by self-assembly of the metal ions templated by mixed anionic species. Magnetic studies revealed remark-

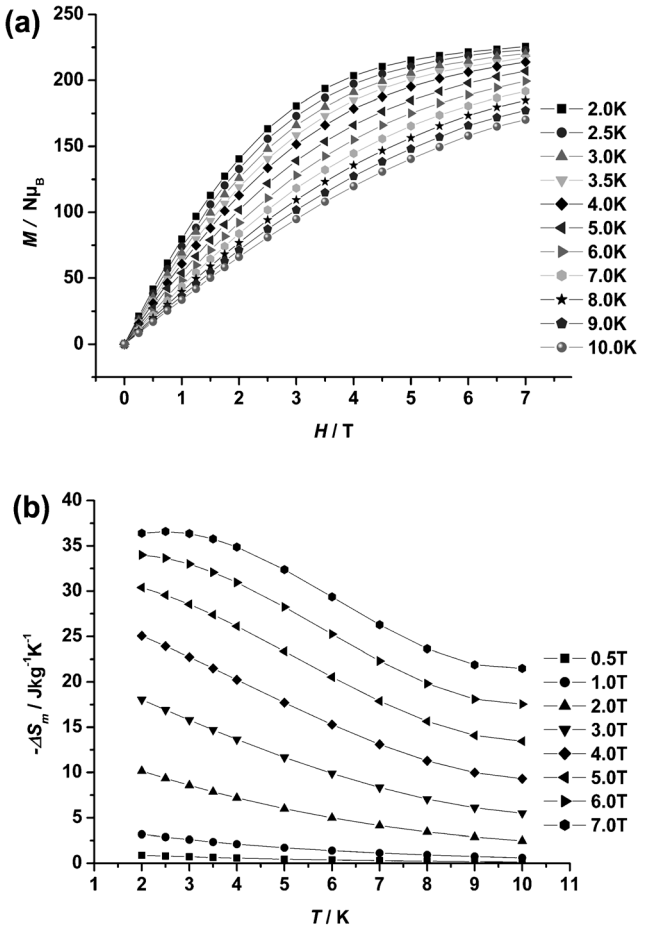

Figure 4. a) Field-dependent magnetization plots at indicated temperatures for **1** and b) ΔS_m calculated by using the magnetization data of **1** at various fields and temperatures.

able changes in entropy with changing magnetic field, and thus high-nuclearity 3d–Gd clusters have great potential for magnetic cooling. The preparation and comparative magnetic studies of clusters of various lanthanide-transition metal combinations with acetate and other small-molecule ligands are in progress with an eye on their eventual applications in magnetic refrigeration.

Experimental Section

Synthesis of **1**: $Ni(CH_3COO)_2{\cdot}6H_2O$ (0.249 g, 1.0 mmol) and $Gd(NO_3)_3{\cdot}6H_2O$ (0.902 g, 2.0 mmol) were added to a mixture of deionized water (5 mL) and anhydrous ethanol (15 mL). The resulting solution was heated to about 70 °C, and a freshly prepared aqueous solution of NaOH (1.0 M) was added dropwise to adjust the pH of the solution to 5–6 while stirring. Then 10 mg of NaCl was added to the solution. After a freshly prepared aqueous solution of NaOH (1.0 M) was added dropwise to the point of incipient but permanent precipitation (pH ≈ 6–6.5), the solution was heated to reflux for 2 h and then filtered. Evaporation of the filtrate under ambient conditions afforded 0.22 g of grassy block-shaped crystals over two weeks (yield 35 % based on Gd). Elemental analysis (%) calcd for $Gd_{36}Ni_{12}C_{36}H_{306}Cl_{11}N_7O_{231}$ (FW = 11 290.35): C 3.83, H 2.73, N 0.87; found: C 3.90, H 2.51, N 0.85; IR (KBr): $\tilde{\nu}$ = 3442 (s), 1637 (w), 1560 (m), 1384 (s), 1121(s), 1108 (m), 636 cm^{-1} (w).

Received: July 22, 2011
Published online: September 16, 2011

Keywords: cluster compounds · lanthanides · magnetic properties · nickel · template synthesis

[1] a) M. Manoli, A. Collins, S. Parsons, A. Candini, M. Evangelisti, E. K. Brechin, *J. Am. Chem. Soc.* **2008**, *130*, 11129; b) M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti, E. K. Brechin, *Angew. Chem.* **2007**, *119*, 4540; *Angew. Chem. Int. Ed.* **2007**, *46*, 4456.

[2] M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. N. Hooper, E. K. Brechin, J. J. Alonso, *Angew. Chem.* **2011**, *123*, 6736; *Angew. Chem. Int. Ed.* **2011**, *50*, 6606.

[3] a) Y. Z. Zheng, M. Evangelisti, R. E. P. Winpenny, *Angew. Chem.* **2011**, *123*, 3776; *Angew. Chem. Int. Ed.* **2011**, *50*, 3692; b) Y. Z. Zheng, M. Evangelisti, R. E. P. Winpenny, *Chem. Sci.* **2011**, *2*, 99; c) G. Karotsis, M. Evangelisti, S. J. Dalgarno, E. K. Brechin, *Angew. Chem.* **2009**, *121*, 10112; *Angew. Chem. Int. Ed.* **2009**, *48*, 9928; d) G. Karotsis, S. Kennedy, S. J. Teat, C. M. Beavers, D. A. Fowler, J. J. Morales, M. Evangelisti, S. J. Dalgarno, E. K. Brechin, *J. Am. Chem. Soc.* **2010**, *132*, 12983.

[4] a) A. Hosoi, Y. Yukawa, S. Igarashi, S. M. Teat, O. Roubeau, M. Evangelisti, E. Cremades, E. Ruiz, L. A. Barrios, G. Aromí, *Chem. Eur. J.* **2011**, *17*, 8264; b) S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti, K. S. Murray, *Chem. Sci.* **2011**, *2*, 1166.

[5] a) M. Evangelisti, E. K. Brechin, *Dalton Trans.* **2010**, *39*, 4672; b) M. Evangelisti, F. Luis, L. J. de Jongh, M. J. Affrote, *Mater. Chem.* **2006**, *16*, 2534.

[6] a) S. Nayak, M. Evangelisti, A. K. Powell, J. Reedijk, *Chem. Eur. J.* **2010**, *16*, 12865; b) J. W. Sharples, Y. Z. Zheng, F. Tuna, E. J. L. McInnes, D. Collison, *Chem. Commun.* **2011**, *47*, 7650; c) J. L. Liu, J. D. Leng, Z. J. Lin, M. L. Tong, *Chem. Asian J.* **2011**, *6*, 1007.

[7] a) C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem.* **2009**, *121*, 155; *Angew. Chem. Int. Ed.* **2009**, *48*, 149; b) W. G. Wang, A. J. Zhou, W. X. Zhang, M. L. Tong, X. M. Chen, M. Nakano, C. C. Beedle, D. N. Hendrickson, *J. Am. Chem. Soc.* **2007**, *129*, 1014; c) T. Liu, Y. J. Zhang, Z. M. Wang, S. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 10500; d) C. E. Anson, A. Eichhöfer, I. Issac, D. Fenske, O. Fuhr, P. Sevillano, C. Persau, D. Stalke, J. Zhang, *Angew. Chem.* **2008**, *120*, 1346; *Angew. Chem. Int. Ed.* **2008**, *47*, 1326; e) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem.* **2004**, *116*, 2169; *Angew. Chem. Int. Ed.* **2004**, *43*, 2117.

[8] a) A. J. Tasiopoulos, W. Wernsdorfer, B. Moulton, M. J. Zaworotko, G. Christou, *J. Am. Chem. Soc.* **2003**, *125*, 15274; b) A. J. Tasiopoulos, T. A. O'Brien, K. A. Abbound, G. Christou, *Angew. Chem.* **2004**, *116*, 349; *Angew. Chem. Int. Ed.* **2004**, *43*, 345.

[9] a) 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; b) X. J. Kong, L. S. Long, Z. P. Zheng, R. B. Huang, L. S. Zheng, *Acc. Chem. Res.* **2010**, *43*, 201.

[10] a) X. M. Chen, S. M. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mak, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 9600; b) J. J. Zhang, T. L. Sheng, M. S. Hu, S. Q. Xia, G. Leibeling, F. Meyer, Z. Y. Fu, L. Chen, R. B. Fu, X. T. Wu, *Chem. Eur. J.* **2004**, *10*, 3963; c) X. J. Kong, Y. L. Wu, L. S. Long, L. S. Zheng, Z. P. Zheng, *J. Am. Chem. Soc.* **2009**, *131*, 6918; d) X. J. Kong, L. S. Long, R. B. Huang, L. S. Zheng, T. D. Harris, Z. P. Zheng, *Chem. Commun.* **2009**, 4354.

[11] Crystal data for **1**: Grassy, block-shaped crystal, orthorhombic, space group *Immm* (no. 71) with a = 20.7546(14), b =

22.3754(16), $c = 35.0986(18)$ Å, $V = 16299.5(18)$ Å^3, $Z = 2$, $\mu = 8.066\ mm^{-1}$, $\rho = 2.300\ g\,cm^{-3}$. Of the 7695 reflections collected on CrysAlis CCD with monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 5158 reflections were observed ($I > 2\sigma(I)$). Based on these and 451 parameters, $R_1 = 0.0746$ ($I > 2\sigma(I)$), $wR_2 = 0.2044$ (all data) were obtained. There are 30 guest water molecules and six Cl^- anions per formula unit. They are severely disordered and were therefore removed by SQUEEZE in structural refinement. CCDC 819911 contains 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.

[12] M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369.

[13] a) Z. P. Zheng, *Chem. Commun.* **2001**, 2521; b) R. Y. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Z. Jin, Z. P. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278.

[14] a) X. J. Kong, Y. P. Ren, L. S. Long, Z. P. Zheng, R. B. Huang, L. S. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 7016; b) X. J. Kong, Y. P. Ren, L. S. Long, Z. P. Zheng, G. Nichol, R. B. Huang, L. S. Zheng, *Inorg. Chem.* **2008**, *47*, 2728.

[15] 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; *Angew. Chem. Int. Ed.* **2008**, *47*, 2398.

