Hydrothermal Synthesis

DOI: 10.1002/ange.200502917

Lanthanide–Transition-Metal Sandwich Framework Comprising $\{Cu_3\}$ Cluster Pillars and Layered Networks of $\{Er_{36}\}$ Wheels[**]

*Jian-Wen Cheng, Jie Zhang, Shou-Tian Zheng,
Man-Bo Zhang, and Guo-Yu Yang**

The design and synthesis of wheel clusters still continues to attract intense interest not only because of their fascinating physical properties but also because of the architectural

---

[*] J.-W. Cheng, Prof. Dr. J. Zhang, S.-T. Zheng, M.-B. Zhang,
Prof. Dr. G.-Y. Yang
State Key Laboratory of Structural Chemistry
and Graduate School of the Fujian Institute
of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, Fujian 350002 (P.R. China)
Fax: (+86) 591-8371-0051
E-mail: ygy@fjirsm.ac.cn

[**] This work was supported by the NNSF of China (Nos. 20271050/20473093), the Talents Program of Chinese Academy of Sciences, and the NSF of Fujian Province (Nos. E0510030/E0210029).

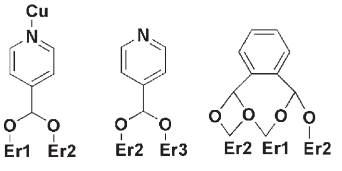
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

beauty of their structures.[1–9] So far, most of the work in this area has focused on the assembly of transition-metal (TM) wheels, thus many high-nuclearity TM wheels have been obtained.[2–8] However, the analogous chemistry of lanthanides is still underdeveloped.[9] As lanthanide ions have variable and high coordination numbers as well as poor stereochemical preferences,[10] the construction of high-nuclearity lanthanide wheels is more difficult than the construction of their TM analogues. In comparison with a number of TM wheels such as $[Mo_{176}]$,[2a] $[Mn_{84}]$,[3a] $[Ni_{24}]$,[4a] $[Fe_{18}]$,[5a] $[Cr_{10}]$,[6a] $[Co_{12}]$,[7a] $[Cu_{10}]$,[8a] $[Ti_8]$,[11a] and $[V_8]$,[11b] only a few lanthanide wheels such as $[Ln_8]$,[9a,b] $[Ln_{10}]$,[9c,d] $[Ln_{12}]$,[9e,f] and $[Ln_{15}]$ have been made.[9e–g]

In general, ligands in the periphery of metal ions play an important role in forming and stabilizing metal wheels or clusters.[3–9,11,12] Recently, we reported a new class of 3D framework that contained $[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}]^{20+}$, $\{Ln_{14}\}$, cores. These compounds were synthesized by choosing isonicotinic acid (Hina) as a bridging ligand to link the $\{Ln_{14}\}$ cores with two types of Cu center.[12] If a second ligand were to be introduced, the cooperativity of both ligands may lead to a new open framework that contains lanthanide clusters different from the $\{Ln_{14}\}$ core, which would be helpful in understanding the formation mechanism of the open framework. In our search for new open frameworks constructed from lanthanide clusters, we have introduced a second ligand, 1,2-benzenedicarboxylic acid (H_2bdc).

We chose H_2bdc as the second ligand based on the following considerations: 1) it has versatile coordination modes;[13] 2) the chelating coordination of bdc may stabilize new lanthanide cluster formed in the crystallization process. Herein, we report two novel coordination polymers, $[Er_7(\mu_3\text{-}O)(\mu_3\text{-}OH)_6(bdc)_3](ina)_9[Cu_3X_4]$ (X = Cl or Br, denoted FJ-2a (**1**) and FJ-2b (**2**), respectively), in which the wheel-shaped building blocks of $[Er_{36}(\mu_3\text{-}OH)_{30}(\mu_3\text{-}O)_6(bdc)_6]^{54+}$, $\{Er_{36}\}$, with an 18 ring is currently the largest lanthanide wheel. **1** and **2** are the first sandwich frameworks based on the links by ina ligands of layered inorganic–organic hybrid polymers, built from nanosized $\{Er_{36}\}$ clusters, and TM clusters. To date, only three TM wheel-cluster polymers constructed from wheel-shaped building blocks are reported, one is a chainlike polymer linked by $\{Mo_{144}\}$ wheels,[2b] the other two are layered polymers linked by $\{Mo_{154}\}$[2c] and $\{Mo_{152}\}$[2d] wheels respectively; no systematic investigation of wheel cluster polymers, in which the metal wheels are linked to each other or linked with metal ions or clusters by organic ligands, has been carried out.

Brown hexagonal crystals of **1** and **2** were made by hydrothermal treatment of Er_2O_3, Hina, H_2bdc, and CuX_2 in water in the presence of $HClO_4$ (pH 2). X-ray crystal-structure analyses reveal that **1** and **2** are isostructural and crystallize in the high-symmetry rhombohedral space group, $R\bar{3}$.[14] Therefore, only the structure of **1** is described in detail. The asymmetric unit of **1** contains three unique Er^{3+}, one Cu^{2+}, and two Cl^- ions, and one bdc and three ina moieties with two coordination modes (see Scheme 1 and the Supporting Information). Er1 and Er2 are eight-coordinate and have bicapped trigonal prism coordination environments: three μ_3-OH groups, one μ_3-O, and two carboxylate oxygen atoms (O_{COO}) from two bridging ina ligands (mode I), and two O_{COO} atoms from one bdc ligand for Er1 (see Supporting Information); two μ_3-OH groups, three O_{COO} atoms from three bridging ina ligands, and three O_{COO} atoms from two bdc ligands for Er2 (see Supporting Information). Six-coordinate Er3 has trigonal-prism coordination geometry: three μ_3-OH groups, and three O_{COO} atoms from three terminal ina ligands with mode II coordination (see Supporting Information). The Er–O bond lengths vary from 2.247(6) to 2.472(7) Å.



Scheme 1. Coordination modes of the ina (I, II) and bdc (III) moieties in **1**.

The Er^{3+} ions are linked by hydroxo and oxo bridges to give two types of small cluster cores: cubic $[Er_4(\mu_3\text{-}O)(\mu_3\text{-}OH)_3]^{7+}$, $\{Er_4\}$, core that contains three Er1 and one Er3 atoms and dimeric $[Er_2(\mu_3\text{-}OH)_2]^{4+}$, $\{Er_2\}$, core that contains two Er2 atoms (Figure 1 a and Supporting Information). Different from the cubane $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$, $[Ln_4]$, which contains four μ_3-OH groups, the $\{Er_4\}$ core in **1** consists of three μ_3-OH groups and one μ_3-O atom, which is rare in known $[Ln_4]$ cores.[9e–g,15] The $\{Er_4\}$ cores link alternately the $\{Er_2\}$ cores to form a nanosized $\{Er_{36}\}$ wheel with 18 ring (Figure 1 b, Supporting Information). Remarkably, six bdc ligands are trapped in the inner of the 18 ring and bond to adjacent Er1 and Er2 atoms by four O_{COO} atoms. Although the bdc ligand has more than fifteen coordination modes,[13,16] it adopts a single μ_5-bdc mode found only in **1**; the number of coordination modes of ina is also reduced from four in $[Ln_{14}]$[12] to two in **1**, which indicates the high cooperativity between the ina and bdc ligands in the formation of **1**; the unique μ_5-bdc mode plays a key role in forming and stabilizing the $\{Er_{36}\}$ wheel (Figure 1 b). It differs from ND-1, in which the 1,2-diaminocyclohexane templates stabilize the 24 ring through hydrogen bonding (see Supporting Information).[17]

Compared with TM wheels, which are formed by TM ions and organic ligands,[3–8] Ln wheels comprise not only organic ligands but also sharing Ln ions.[9] In $[Ln_8]/[Ln_{10}]$ wheels,[9a–d] the Ln ions are linked by OC_2H_4OMe ligands to form an 8/10 ring in which the center is empty. In $[Ln_{12}]/[Ln_{15}]$ wheels,[9e–g] four/five $\{Ln_4\}$ cores share Ln vertices to form a 4 /5 ring around 1 or 2 halide ions in their central cavity. Notably, the construction mode of the wheel-shaped $\{Er_{36}\}$ cluster in **1** is significantly different from above discrete TM or Ln wheels.[3–9] The $\{Er_{36}\}$ wheel is made up of strictly alternating $\{Er_4\}$ and $\{Er_2\}$ cores that share μ_3-OH groups (Figure 1 a, Supporting Information); the bdc ligands trapped in the 18 ring further stabilize the $\{Er_{36}\}$ wheel (Figure 1 b). Additionally, bdc ligands are grouped into threes to form triangles that are stacked along the *ab*-plane in a staggered fashion and thus appear as hexagons with an empty center in a 2D projection (Figure 1 b). Each $\{Er_{36}\}$ cluster is linked to surrounding clusters by sharing -Er1-OH-$\{Er2\}_2$-OH-Er1-

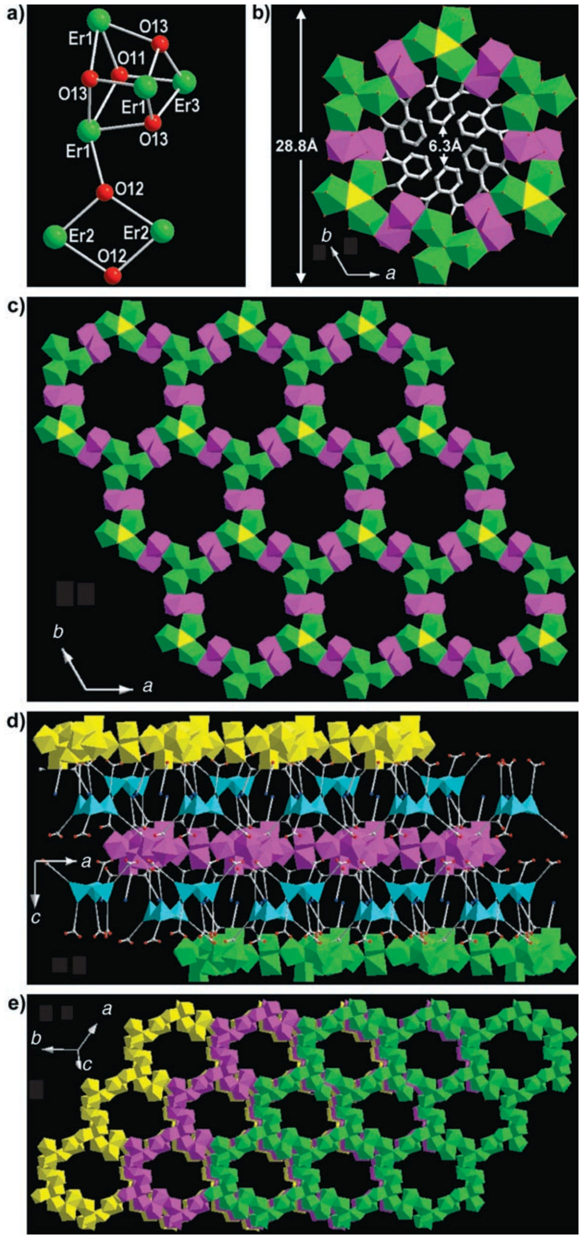


Figure 1. a) The linkage of $\{Er_4\}$ and $\{Er_2\}$ cores through μ_3-OH in **1**. b) View of the $\{Er_{36}\}$ wheel showing the bdc ligands near the walls of the 18 ring. The hollow center of the 18 ring has a diameter of about 6.3 Å. Polyhedra centered by Er1 (green), Er2 (purple), and Er3 (yellow). c) View of giant wheel clusters linked to form layered cluster network with 18 ring by an Er1-OH-$\{Er2\}_2$-OH-Er1 bridge. The bdc ligands are omitted for clarity; color scheme as in (b). d) View of sandwich framework based on linkages of 2D cluster layers and $\{Cu_3Cl_4\}$ cluster pillars by ina ligands. Three adjacent layers of $\{Er_{36}\}$ wheels are represented in green, purple, and yellow, $\{Cu_3Cl_4\}$ in cyan; white lines stand for pyridine rings of ina ligands; bdc ligands are omitted for clarity. e) View of the channels in **1** along the [211] direction. Color scheme as in (d); $\{Cu_3Cl_4\}$ cores, ina and bdc ligands are omitted for clarity.

bridges (see Supporting Information), thus forming a highly-ordered layered cluster network with hexagonal, honeycomb arrays (Figure 1c and Supporting Information). The layered hybrid networks are stacked in parallel with -ABCABC- alternations along the *c* axis, each layer is shifted by $(-\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c})/3$ with respect to the next one (Figure 1d, Supporting Information). The distance between adjacent layers is 8.3 Å.

In **1**, the five-coordinate Cu center has a nearly square-pyramidal coordination environment made up of one μ_3-Cl, two μ_2-Cl, and two N atoms from two bridging ina moieties (see Supporting Information). Three Cu ions are bridged by three μ_2-Cl and one μ_3-Cl atoms to form a $\{Cu_3Cl_4\}$ trimeric cluster (Cu···Cu 4.578(3) Å; μ_2-Cl–Cu 2.378(3)/2.712(4) Å; μ_3-Cl–Cu 2.707(2) Å, which is slightly longer than the μ_3-Cl–Cu bond length (2.576 Å) in a [Cu_3Cl] cluster containing a Cl^- ligand in trigonal planar coordination mode, N–Cu 1.940(10)/1.967(9) Å.[18] Each $\{Cu_3Cl_4\}$ core caps the $\{Er_{36}\}$ cluster by three ina ligands that contain N1/O1/O2 atoms and link the $\{Er_4\}$ core of the adjacent staggered lanthanide cluster layers by another three ina ligands comprising N3/O5/O6 atoms (see Supporting Information). Thus, the $\{Cu_3Cl_4\}$ core links six ina ligands to form a new cluster $\{Cu_3Cl_4(ina)_6\}$ pillared between adjacent lanthanide cluster layers (Figure 1d and Supporting Information). While each $\{Er_{36}\}$ cluster links eight $\{Cu_3Cl_4\}$ cores through ina ligands (Supporting Information): two $\{Cu_3Cl_4\}$ cores cap two sides of the $\{Er_{36}\}$ cluster; six $\{Cu_3Cl_4\}$ cores link six $\{Er_4\}$ cores on two sides of the $\{Er_{36}\}$ cluster. The $\{Cu_3Cl_4\}$ cores at two sides of the $\{Er_{36}\}$ cluster have reverse orientation and are stacked along the *c* axis in a staggered fashion and thus appear as small and large hexagons on a 2D projection (see Supporting Information).

The linkages between 2D hybrid cluster polymers and $\{Cu_3Cl_4\}$ clusters by ina ligands give rise to an unprecedented 3D sandwich framework (Figure 1d and Supporting Information) with channels along the [211], $[1\bar{1}\bar{1}]$, $[12\bar{1}]$, $[\bar{2}2\bar{1}]$, $[42\bar{1}]$, $[45\bar{1}]$, [241], $[15\bar{1}]$, $[1\bar{4}\bar{1}]$, [541], and [511] directions (Figure 1e and Supporting Information). As many as 54 ina ligands bond to the $\{Er_{36}\}$ cluster: 36 ina ligands (mode I) bridge and link the $\{Er_{36}\}$ cluster with the $\{Cu_3Cl_4\}$ core through O_{COO} and N atoms; eighteen ina ligands (mode II) are terminal and only bond to six Er3 atoms of the $\{Er_{36}\}$ cluster through O_{COO} atoms, the N atoms are free and are directed into the center of the channels (Figure 1d and Supporting Information). Thus, the structure is of strictly alternating lanthanide cluster hybrid layers and the $\{Cu_3Cl_4\}$ cores bridged by ina ligands of mode I coordination to form a 3D framework, in which the $\{Cu_3Cl_4\}$ cores located between adjacent layers have opposite orientations along the *c* axis (Figure 1d). It is also understood that the lanthanide cluster hybrid layers are pillared by the clusters of $\{Cu_3Cl_4(ina)_6\}$ to form a 3D sandwich framework.

The DC magnetic susceptibility of **1** was measured in the temperature range of 2–300 K under an applied magnetic field of 0.5 T. The μ_{eff} value per molecule is 24.4 μ_B at room temperature, which is less than the calculated value of 25.5 μ_B for seven Er^{3+} and three Cu^{2+} ions without magnetic interaction, and thus it suggests a possible presence of antiferromagnetic couplings between the metal ions (Er···Er and/or Cu···Cu). As the temperature is lowered, **1** shows a continuous decrease in the value of μ_{eff}, which reaches 15.4 μ_B at 2 K. This behavior may be attributed to the crystal-field splitting of the Er^{3+} ion and the contribution of overall antiferromagnetic interactions.[19] No magnetic ordering and frequency dependence was observed above 2 K from the variable-temperature AC magnetic susceptibility measurements (see Supporting Information).

In summary, we have made two novel 3D lanthanide–TM coordination polymers, each with a sandwich framework, under hydrothermal conditions from ina and bdc ligands. The unique μ_5-bdc coordination in the structure plays a key role in forming and stabilizing the $\{Er_{36}\}$ cluster. The linkages between the layered $\{Er_{36}\}$ cluster networks and the $\{Cu_3\}$ clusters through ina ligands result in two unusual lanthanide–TM open frameworks with multidirectional channels. To the best of our knowledge, this is the first time that such sandwich frameworks, made of nanosized $\{Er_{36}\}$ cluster polymeric layers and TM cluster pillars have been obtained. The unique cooperativity between the ina and the bdc ligands in the growth of **1** and **2** suggests that "synergistic coordination" as a useful synthetic strategy has potential application in the design and synthesis of molecular materials.

Experimental Section

1 and **2**: A mixture of Er_2O_3 (0.5 mmol, 0.191 g), Hina (2 mmol, 0.246 g), H_2bdc (1.0 mmol, 0.168 g), CuX_2 ($CuCl_2\cdot 2H_2O$, 0.2 mmol, 0.034 g; $CuBr_2$, 0.2 mmol, 0.045 g), H_2O (10 mL), and $HClO_4$ (0.385 mmol) (pH 2) was sealed in a 30 mL Teflon-lined bomb at 170 °C for 7 days then slowly cooled to room temperature. Brown prismatic crystals of **1** and **2** were recovered by filtration, washed by distilled water, and air-dried (Yield: 25 % and 21 % based on $CuCl_2\cdot 2H_2O$ and $CuBr_2$ for **1** and **2**, respectively). The positions of the diffraction peaks of the experimental and simulated XRD patterns corresponded well, thus indicating phase purity of the as-synthesized samples of **1** and **2** (see Supporting Information). Elemental analysis calcd (%) for $C_{78}H_{54}Cl_4Cu_3Er_7N_9O_{37}$ (**1**): C 29.16, H 1.70, N 3.92; found: C 29.21, H 2.21, N 3.65; for $C_{78}H_{54}Br_4Cu_3Er_7N_9O_{37}$ (**2**): C 27.63, H 1.61, N 3.72; found: C 28.17, H 2.08, N 3.69. EDAX gives the Cu/Cl/Er ratio in **1** as 3:3.8:6.8 (calcd Cu/Cl/Er = 3:4:7) and the Cu/Br/Er ratio in **2** as 3:4.1:7.2 (calcd Cu/Br/Er = 3:4:7). These results are in agreement with the formulas of **1** and **2** found from the single-crystal analysis. Thermogravimetric analysis indicated that **1** was stable in air up to 200 °C. Between 200 and 600 °C, weight loss corresponding to loss of ina and bdc ligands was observed.

Received: August 16, 2005

Keywords: bridging ligands · cluster compounds · copper · hydrothermal synthesis · lanthanides

---

[1] a) K. L. Taft, C. D. Delfs, G. C. Apaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *116*, 823; b) L. J. De Jongh, A. R. Miedema, *Adv. Phys.* **1974**, *23*, 1; c) C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203.

[2] a) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* **1998**, *110*, 1278; *Angew. Chem. Int. Ed.* **1998**, *37*, 1220; b) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtmann, F. Peters, C. Carsten, J. Meyer, *Angew. Chem.* **1997**, *109*, 500; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 484; c) A. Müller, S. K. Das, H. Bögge, C. Beugholt, M. Schmidtmann, *Chem. Commun.* **1999**, 1035; d) A. Müller, E. Krichemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, S. K. Das, F. Peters, *Chem. Eur. J.* **1999**, *5*, 1496, and references therein.

[3] a) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem.* **2004**, *116*, 2169; *Angew. Chem. Int. Ed.* **2004**, *43*, 2117, and references therein; b) M. Murugesu, J. Raftery, W. Wernsdorfer, G. Christou, E. K. Brechin, *Inorg. Chem.* **2004**, *43*, 4203, and references therein.

[4] a) A. L. Dearden, S. Parsons, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 155; *Angew. Chem. Int. Ed.* **2001**, *40*, 151, and references therein; b) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Commun.* **2001**, 2666.

[5] a) S. P. Watton, R. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati, S. J. Lippard, *Angew. Chem.* **1997**, *109*, 2917; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2774, and references therein; b) O. L. Sydora, P. T. Woleczanski, E. B. Lobkovsky, *Angew. Chem.* **2003**, *115*, 2789; *Angew. Chem. Int. Ed.* **2003**, *42*, 2685, and references therein; c) L. F. Jones, A. Batsanov, E. K. Brechin, D. Collison, M. Helliwell, T. Mallah, E. J. L. McInnes, S. Piligkos, *Angew. Chem.* **2002**, *114*, 4494; *Angew. Chem. Int. Ed.* **2002**, *41*, 4318, and references therein.

[6] E. J. L. McInnes, C. Anson, A. K. Powell, A. J. Thomson, S. Poussereau, R. Sessoli, *Chem. Commun.* **2001**, 89, and references therein.

[7] E. K. Brechin, O. Cador, A. Caneschi, C. Cadiou, S. G. Harris, S. Parsons, M. Vonci, R. E. P. Winpenny, *Chem. Commun.* **2002**, 1860, and references therein.

[8] a) C.-H. Chang, K.-C. Hwang, C.-S. Liu, Y. Chi, A. J. Carty, L. Scoles, S.-M. Peng, G.-H. Lee, J. Reedijk, *Angew. Chem.* **2001**, *113*, 4787; *Angew. Chem. Int. Ed.* **2001**, *40*, 4651; b) G. A. Ardizzoia, M. A. Angaroni, G. L. Monica, F. Cariati, S. Cenini, M. Moret, N. Masciocchi, *Inorg. Chem.* **1991**, *30*, 4347.

[9] a) J. Xu, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 2857; *Angew. Chem. Int. Ed.* **2000**, *39*, 2745, and references therein; b) T. Kajiwara, H. Wu, T. Ito, N. Iki, S. Miyano, *Angew. Chem.* **2004**, *116*, 1868; *Angew. Chem. Int. Ed.* **2004**, *43*,1832; c) L. G. Westin, M. Kritikos, A. Caneschi, *Chem. Commun.* **2003**, 1012; d) O. Poncelet, L. G. Hubert-Pfalzgraf, J.-C. Daran, R. Astier, *J. Chem. Soc. Chem. Commun.* **1989**, 1846; e) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278; f) Z. Zheng, *Chem. Commun.* **2001**, 2521; g) R. Wang, Z. Zheng, T. Jin, R. J. Staples, *Angew. Chem.* **1999**, *111*, 1929; *Angew. Chem. Int. Ed.* **1999**, *38*, 1813; h) R. Anwander, *Angew. Chem.* **1998**, *110*, 619; *Angew. Chem. Int. Ed.* **1998**, *37*, 599.

[10] a) F. Renaud, C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Am. Chem. Soc.* **1999**, *121*, 9326; b) M. R. Bürgstein, M. T. Gamer, P. W. Roesky, *J. Am. Chem. Soc.* **2004**, *126*, 5213.

[11] a) H. Barrow, D. A. Brown, N. W. Alcock, H. J. Clase, M. G. H. Wallbridge, *J. Chem. Soc. Chem. Commun.* **1995**, 1231; b) H. Kumagai, S. Kitagawa, *Chem. Lett.* **1996**, 471.

[12] M.-B. Zhang, J. Zhang, S.-T Zheng, G.-Y. Yang, *Angew. Chem.* **2005**, *117*, 1409; *Angew. Chem. Int. Ed.* **2005**, *44*, 1385, and references therein.

[13] Y. Wan, L. Jin, K. Wang, L. Zhang, X. Zheng, S. Lu, *New J. Chem.* **2002**, *26*, 1590.

[14] Crystal data for **1**: $C_{78}H_{54}Cl_4Cu_3Er_7N_9O_{37}$, $M_r = 3212.54$, rhombohedral, $R\bar{3}$, $a = 18.2829(18)$, $c = 47.823(8)$ Å, $V = 13\,844(3)$ Å^3, $Z = 6$, $\rho = 2.312$ g cm^{-3}, $\mu = 7.171$ mm^{-1}, $F(000) = 9072$, GOF = 1.153. A total of 35 759 reflections were collected and 7047 are unique ($R_{int} = 0.0717$). $R1/wR2 = 0.0587/0.1457$ for 6808 reflections ($I > 2\sigma(I)$) and 408 parameters. **2**: $C_{78}H_{54}Br_4Cu_3Er_7N_9O_{37}$, $M_r = 3390.38$, rhombohedral, $R\bar{3}$, $a = 18.3057(2)$, $c = 48.1567(3)$ Å, $V = 13\,975.3(2)$ Å^3, $Z = 6$, $\rho = 2.417$ g cm^{-3}, $\mu = 8.705$ mm^{-1}, $F(000) = 9504$, GOF = 1.038. A total of 36 111 reflections were collected and 7121 are unique ($R_{int} = 0.0922$).

$R1/wR2 = 0.0401/0.1044$ for 415 parameters and 6184 reflections ($I > 2\sigma(I)$). The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed by using the multiscan program. The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program.[20] All non-hydrogen atoms, except N2, disordered C11/C11′ and C12/C12′ in **1** and **2**, were refined anisotropically. CCDC-279324 (**1**) and -279325 (**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.

[15] a) B. Ma, D. Zhang, S. Gao, T. Jin, C. Yan, G. Xu, *Angew. Chem.* **2000**, *112*, 3790; *Angew. Chem. Int. Ed.* **2000**, *39*, 3644; b) R. Wang, H. Liu, M. D. Carducci, T. Jin, C. Zheng, Z. Zheng, *Inorg. Chem.* **2001**, *40*, 2743.

[16] a) C. Canada-Vilalta, M. Pink, G. Christou, *Dalton Trans.* **2003**, 1121, and references therein; b) Y.-S. Song, B. Yang, *Inorg. Chim. Acta* **2005**, *358*, 191.

[17] G.-Y. Yang, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 8389.

[18] G. Seeber, P. Kogerler, B. M. Kariukj, L. Cronin, *Chem. Commun.* **2004**, 1580.

[19] a) J.-P. Costes, J. M. Clemente-Juan, F. Dahan, F. Nicodème, M. Verelst, *Angew. Chem.* **2002**, *114*, 333; *Angew. Chem. Int. Ed.* **2002**, *41*, 323; b) G. Xu, Z. Wang, Z. He, Z. Lu, C. Liao, C. Yan, *Inorg. Chem.* **2002**, *41*, 6802.

[20] G. M. Sheldrick, SHELXTL-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**.