Inorg. Chem. **2007**, *46*, 3212–3216

Inorganic Chemistry
Article

Surface Modification of High-Nuclearity Lanthanide Clusters: Two Tetramers Constructed by Cage-Shaped {Dy_{26}} Clusters and Isonicotinate Linkers

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Received December 3, 2006

By incorporation of NO_3^- ligands with trigonal planar geometry as surface modifiers into the lanthanide cluster core backbone to remarkably improve the dimension of cluster cores, two novel lanthanide cluster compounds, $Dy_{30}I(\mu_3\text{-}OH)_{24}(\mu_3\text{-}O)_6(NO_3)_9(IN)_{41}(OH)_3(H_2O)_{38}$ (**1**) and $Dy_{104}I_4(\mu_3\text{-}OH)_{80}(\mu_3\text{-}O)_{24}(NO_3)_{36}(IN)_{125}(OH)_{19}(H_2O)_{167}$ (**2**) (HIN = isonicotinic acid), have been obtained under hydrothermal conditions. Single-crystal X-ray diffraction shows that in both cluster compounds, the block blocks of $[Dy_{26}(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9I]^{36+}$, {$Dy_{26}$}, are the largest cage-shaped lanthanide cluster cores known. Compound **1** is the first tetramer based on the linkage of two different types of high-nuclearity lanthanide clusters and IN ligands, while compound **2** represents the first tetramer constructed by {Dy_{26}} clusters and IN linkers.

Introduction

High-nuclearity clusters have received intense interest because of their intriguing variety of architectures and potential applications in various aspects such as magnetism, optics, electronics, and catalysis.[1] To date, many large transition metal clusters, such as molybdenum,[2] silver,[3] manganese,[4] and copper clusters,[5] have been synthesized. In contrast, the analogous chemistry of lanthanides is still underdeveloped because of some intrinsic characteristics of lanthanide ions such as the high, variable coordination numbers and the small energy difference between various coordination geometries.[6] The general strategy for the synthesis of high-nuclearity lanthanide clusters is to control the hydrolysis of metal ions in the presence of supporting ligands, and the reported structures include tetra-,[6e] penta-,[7] hexa-,[8] hepta-,[9] octa-,[6a] nona-,[10] deca-,[11] dodeca-,[12] tetra-

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deca-,[6b,13] and pentadecanuclear[6d,12] lanthanide clusters. Recently, a cluster polymer unit based on a hexatriacontanuclear wheel cluster has been reported.[14] Despite the synthetic progress of high-nuclearity lanthanide clusters, this mono-route toward the ligand-controlled hydrolysis seems inappropriate to remarkably improve the dimension of these cluster cores because it is difficult to incorporate more lanthanide centers into one cluster to satisfy the cooperativity among different lanthanide centers. Furthermore, another factor, probably the most important aspect, is that the high-nuclearity clusters possess a high positive charge and are very unstable in solution, which easily leads to the formation of polymeric lanthanide hydroxide precipitates.[6c] It is natural to come up with such an idea: the incorporation of surface modifiers such as small multidenate anion ligands into one cluster core backbone results in the positive charge on the cluster core decreasing and the cluster thus being stabilized; furthermore, the cluster core surface expands, which permits more lanthanide ions to incorporate into the cluster core, as a sequence, generating a lanthanide cluster with higher nuclearity with the help of supporting ligands. We believe that this directed assemby by surface modifers should be an excellent strategy for the preparation of nanosized high-nuclearity lanthanide clusters with novel properties associated with the quantum size effect.

In the current work, we chose NO_3^- as a surface modifier on the basis of the following considerations: (i) it is a multidenate ligand with versatile coordination,[15] (ii) it has a strong affinity toward lanthanide ions based on the hard−soft acid base classification,[6] and (iii) the unique trigonal planar geometry allows NO_3^- ligands to be used as potential expanders to expand the cluster core surface, which leads to more lanthanide ions being incorporated in the cluster. On the other hand, a linear multifunctional ligand with nitrogen and oxygen donors, isonicotinic acid (HIN) was selected as a supporting ligand to construct high-nuclearity lanthanide clusters. Herein, we report two lanthanide cluster compounds, $Dy_{30}I(\mu_3\text{-}OH)_{24}(\mu_3\text{-}O)_6(NO_3)_9(IN)_{41}(OH)_3(H_2O)_{38}$ (**1**) and $Dy_{104}I_4(\mu_3\text{-}OH)_{80}(\mu_3\text{-}O)_{24}(NO_3)_{36}(IN)_{125}(OH)_{19}(H_2O)_{167}$ (**2**), in which the blocks of $[Dy_{26}(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9I]^{36+}$, $\{Dy_{26}\}$, are the largest known cage-shaped lanthanide clusters. Furthermore, compound **1** is the first tetramer based on the linkage of two different types of lanthanide clusters and IN linkers, and compound **2** represents the first tetramer constructed by $\{Dy_{26}\}$ clusters and IN linkers.

Experimental Section

Materials and General Methods. All chemicals were of reagent grade and were used without further purification. Distilled water was used in all reactions. The elemental analyses (C, H, and N) were carried out a Perkin-Elmer 240C elemental analyzer. The infrared spectra were recorded (400-4000 cm^{-1} region) on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on an SDT Q600 instrument in a flowing nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Table 1. Crystal Data and Structure Refinement for Compounds **1** and **2**

	1	**2**
empirical formula	$C_{246}H_{267}Dy_{30}IN_{50}O_{180}$	$C_{750}H_{933}Dy_{104}I_4N_{161}O_{648}$
fw	11806.00	39979.18
temp (K)	293	188
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	23.000(6)	37.962(2)
b (Å)	24.256(6)	39.630(3)
c (Å)	63.560(16)	42.080(3)
α (deg)	90	90.1890(10)
β (deg)	95.462(5)	93.5050(10)
γ (deg)	90	109.6040(10)
V (Å^3)	35 399(16)	59 506(6)
Z	4	2
ρ_{calcd} (g cm^{-3})	2.222	2.231
μ (mm^{-1})	6.454	6.648
$F(000)$	22264	37640
GOF	1.012	0.962
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0504	0.0713
$R_2{}^b$ [$I > 2\sigma(I)$]	0.1117	0.1326

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Synthesis of $Dy_{30}I(\mu_3\text{-}OH)_{24}(\mu_3\text{-}O)_6(NO_3)_9(IN)_{41}(OH)_3(H_2O)_{38}$ (1). A mixture of Dy_2O_3 (0.187 g, 0.5 mmol), AgI (0.167 g, 0.5 mmol), HIN (0.246 g, 2.0 mmol), HNO_3 (0.037 g, 0.5 mmol), and H_2O (15 mL) was placed into a 23 mL Teflon reactor and kept under autogenous pressure at 150 °C for 10 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and yellow crystals were obtained (42% yield based on Dy). Anal. Calcd (%) for $C_{246}H_{267}Dy_{30}IN_{50}O_{180}$: C, 25.00; H, 2.26; N, 5.93. Found: C, 24.56; H, 1.84; N, 6.3. IR (KBr pellet, cm^{-1}): 3420 (m), 1608(s), 1549(s), 1413(s), 1209(w), 1056(w), 1006(w), 776(m), 674(m).

Synthesis of $Dy_{104}I_4(\mu_3\text{-}OH)_{80}(\mu_3\text{-}O)_{24}(NO_3)_{36}(IN)_{125}(OH)_{19}(H_2O)_{167}$ (2). A mixture of Dy_2O_3 (0.187 g, 0.5 mmol), AgI (0.167 g, 0.5 mmol), HIN (0.123 g, 1.0 mmol), HNO_3 (0.047 g, 0.75 mmol), and H_2O (15 mL) was placed into a 23 mL Teflon reactor and kept under autogenous pressure at 180 °C for 8 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and deep yellow crystals were obtained (31% yield based on Dy). Anal. Calcd (%) for $C_{750}H_{933}Dy_{104}I_4N_{161}O_{648}$: C, 22.51; H, 2.33; N, 5.64. Found: C, 22.31; H, 1.84; N, 6.09. IR (KBr pellet, cm^{-1}): 3413(m), 1602(s), 1542(s), 1412(s), 1217(w), 1055(w), 1005(w), 767(m), 680(m).

X-ray Crystallographic Study. The collection of crystallographic data of **1** was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K, while the crystallographic data of **2** were collected on the same diffractometer at 188 K. The empirical absorption correction was applied. These structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.[17] The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1.

Results and Discussion

Crystal Structure of $Dy_{30}I(\mu_3\text{-}OH)_{24}(\mu_3\text{-}O)_6(NO_3)_9(IN)_{41}(OH)_3(H_2O)_{38}$ (1). Single-crystal X-ray diffraction analysis

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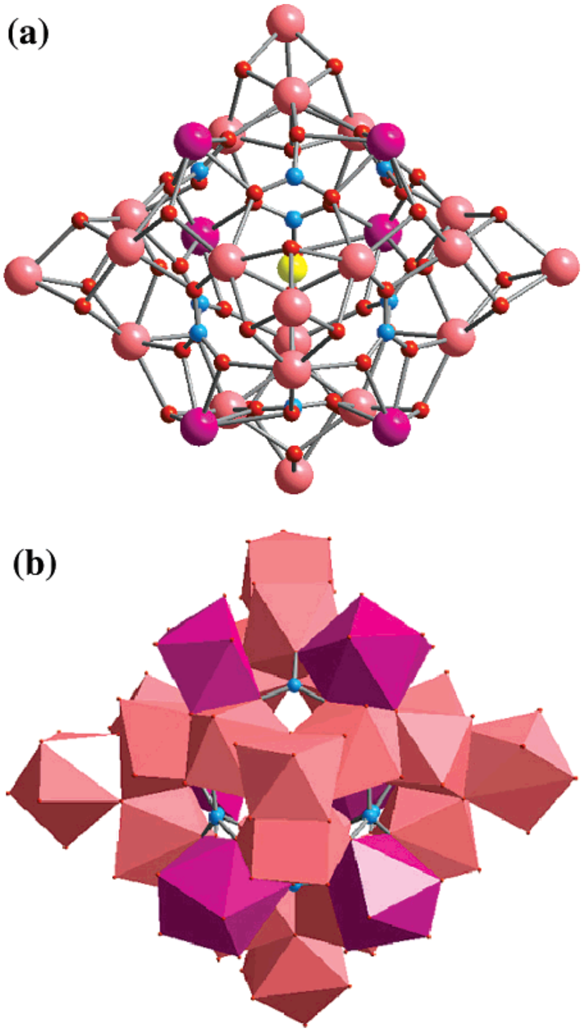


Figure 1. (a) View of the structure of $\{Dy_{26}\}$ core in **1**. (b) Polyhedral representation of the structure of $\{Dy_{26}\}$ cluster in **1**. The color codes are as follows: Dy (Dy1−Dy20) in the cubane-like $\{Dy_4\}$ cores, brick red; Dy (Dy21−Dy26), purple; N, blue; O, red; I, yellow.

reveals that **1** crystallizes in monoclinic space group $P2_1/c$ and exhibits a fascinating tetramer consisting of two $\{Dy_{26}\}$ clusters and two $\{Dy_4\}$ clusters. There is one $[Dy_{26}(\mu_3\text{-}OH)_{20}(\mu_3\text{-}O)_6(NO_3)_9I]^{36+}$ core, one $[Dy_4(\mu_3\text{-}OH)_4]^{8+}$ core, forty-one IN ligands, three OH anions, and thirty-eight H_2O molecules in an asymmetric unit. As shown in Figure 1a, the $\{Dy_{26}\}$ core is constructed by a cage consisting of twenty-six Dy ions and one I ion. Nine NO_3^- ligands are incorporated into the cluster core backbone by Dy−O coordination bonds. For clarity, the large $\{Dy_{26}\}$ cluster can be regarded as an assembly of cubane-like $[Dy_4(\mu_3\text{-}OH)_4]^{8+}$ ($\{Dy_4\}$) clusters, which are common in lanthanide hydroxo/oxo clusters,[6d ,9,12] and additional Dy centers: five edge-sharing $\{Dy_4\}$ clusters are assembled into a $\{Dy_{20}\}$ cluster, furthermore, other Dy centers (Dy21, Dy22, Dy23, Dy24, Dy25, and Dy26) and the $\{Dy_{20}\}$ cluster construct the $\{Dy_{26}\}$ cluster by sharing μ_3-O atoms and the oxygen atoms from the NO_3^- ligands (Figures 1b and S1). The size of the $\{Dy_{26}\}$ cluster is 20.47 × 17.20 Å^2 (as measured between the centers of opposite coordination oxygen atoms).

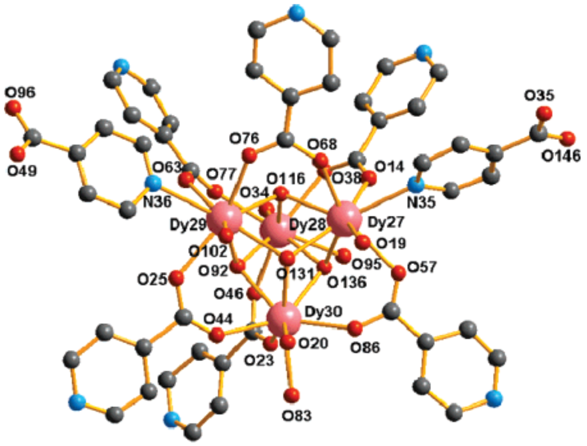
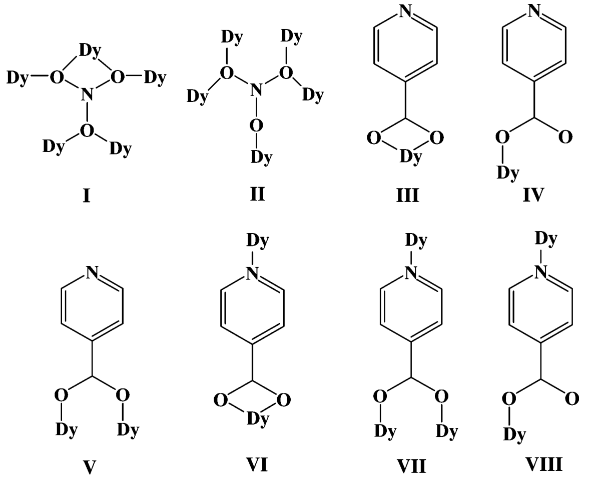


Figure 2. View of the whole structure of another crystallographically independent $\{Dy_4\}$ cluster containing Dy27, Dy28, Dy29, and Dy30 centers in **1**: C, gray; other color codes as in Figure 1.

Chart 1. Coordination Modes of NO_3^- (**I**, **II**) and IN (**III**−**VIII**) Ligands in **1** and **2**



There are three types of connecting modes between the $\{Dy_4\}$ clusters and other Dy centers (Dy21, Dy22, Dy23, Dy24, Dy25, and Dy26) in the $\{Dy_{26}\}$ cluster (Figures 1 and S2). Each of the Dy21, Dy24, and Dy26 centers is connected to one $\{Dy_4\}$ cluster by two oxygen atoms from two NO_3^- ligands, while each of Dy22, Dy23, and Dy25 centers shares one $\{Dy_4\}$ cluster via one oxygen atom from one NO_3^- ligand. Moreover, each of these six Dy centers is also connected to two edge-sharing $\{Dy_4\}$ clusters by one μ_3-O atom and two oxygen atoms from two NO_3^- ligands.

As shown in Chart 1 (**I**), each NO_3^- ligand coordinates to five Dy centers in the $\{Dy_{26}\}$ cluster. This full coordination mode of the NO_3^- ligand has not yet been reported so far, and it plays an important role in the expansion of the cluster core surface and stabilization of the cluster. Compared to the reported high-nuclearity clusters such as $[Dy_{12}(\mu_3\text{-}OH)_{16}I_2(\mu_3\text{-}Tyr)_8(H_2O)_{20}]^{10+}$ and $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(\mu_3\text{-}Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5(H_2O)_{18}]^{12+}$ built up from cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ units,[12] the $\{Dy_{26}\}$ cluster in **1** consists of more cubane-like $\{Dy_4\}$ clusters, which structurally embodies its higher core surface.

In the structure of **1**, there is another crystallographically unique cubane-like $\{Dy_4\}$ cluster, which is composed of Dy27, Dy28, Dy29, and Dy30 centers (Figure 2). In this $\{Dy_4\}$ cluster, each of Dy27 and Dy29 centers is eight

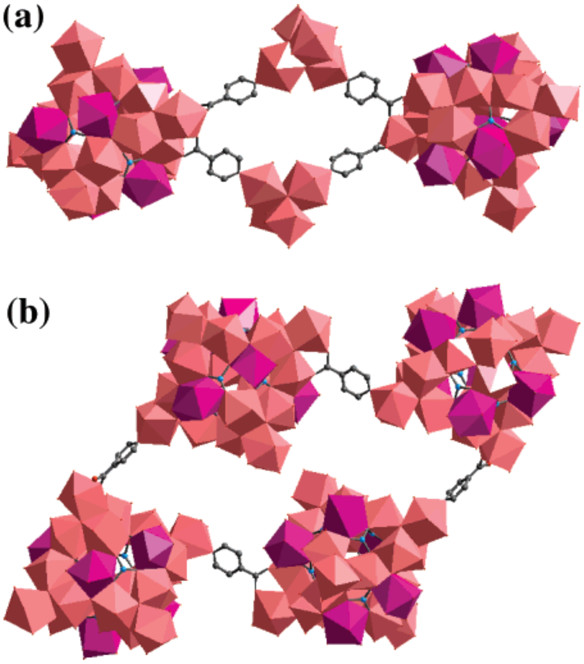


Figure 3. (a) View of the structure of tetramer constructed by two types of lanthanide clusters ({Dy_{26}} and {Dy_4}) and IN linkers in **1**. (b) View of the structure of tetramer constructed by {Dy_{26}}-1 and {Dy_{26}}-2 clusters and IN linkers in **2**. The pyridine rings in terminal IN ligands are omitted for clarity. Color codes as in Figure 2.

coordinated by one nitrogen atom from one bridging IN ligand, three oxygen atoms from three terminal IN ligands, one oxygen atom from one water molecule, and three μ_3-OH groups. Each of the Dy28 and Dy30 centers is eight coordinated by three oxygen atoms from three terminal IN ligands, two oxygen atoms from two water molecules, and three μ_3-OH groups. It should be noted that the Dy centers in the {Dy_{26}} cluster display various coordination environments because of the high-nuclearity and asymmetry of this large cluster (Figure S3 in the Supporting Information). In the five {Dy_4} clusters, except the Dy8 center with a nine-coordinated environment, the remaining nineteen Dy centers are all eight coordinate, while among the Dy centers which are not in those {Dy_4} clusters, Dy22, Dy23, and Dy25 centers are eight coordinate and Dy21, Dy24, and Dy26 centers are nine coordinate.

It is interesting that the {Dy_{26}} and {Dy_4} clusters are linked by IN ligands to form a tetramer with a rhombic shape (Figure 3a). The rhombus size is 28.40 × 25.11 Å. To our knowledge, this compound represents the first example of tetramer constructed by two different high-nuclearity lanthanide clusters. Because of the high-nuclearity of {Dy_{26}} cluster, 35 IN ligands coordinate to this core through the carboxylate oxygen atoms (Figure 4). Chart 1 (**III**−**VII**) illustrates five coordination modes of the IN ligands in **1**. Seven IN ligands with mode **III**, four IN ligands with mode **IV**, and twenty-two IN ligands with mode **V** are terminal and coordinate to the {Dy_{26}} core through the carboxylate oxygen atoms. Two bridging IN ligands with modes **VI** and **VII** also coordinate to the {Dy_{26}} core through the carboxylate oxygen atoms, while the pyridyl nitrogen atoms in those bridging IN ligands atoms coordinate to another unique {Dy_4} core in the tetramer. Moreover, six terminal IN ligands with mode **V** and two bridging IN ligands with modes **VI** and **VII** coordinate to this {Dy_4} core through the carboxylate oxygen atoms and pyridyl nitrogen atoms (Figure 2). Therefore, the structure can be understood that {Dy_{26}} and {Dy_4} clusters are bridged by four IN ligands with modes **VI** and **VII** to form a tetramer. Because of the existence of many H_2O molecules in the crystal structure, a 3D supramolecular network forms through the strong hydrogen bond interactions.

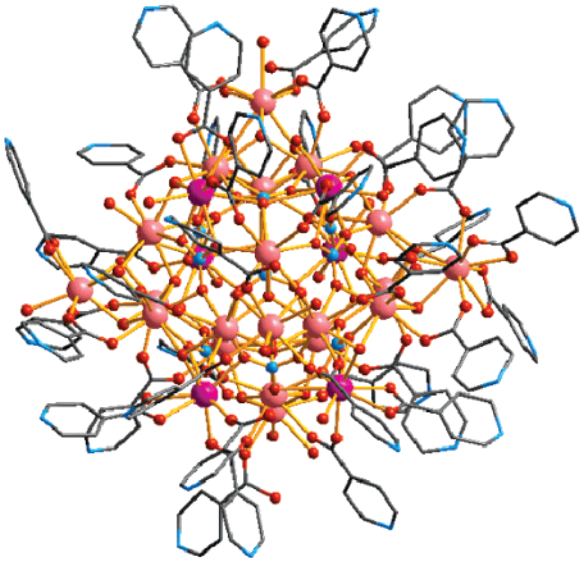


Figure 4. View of the structure of {Dy_{26}} cluster containing 35 IN ligands in **1**. Color codes as in Figure 2.

Crystal structure of $Dy_{104}I_4(\mu_3\text{-OH})_{80}(\mu_3\text{-O})_{24}(NO_3)_{36}(IN)_{125}(OH)_{19}(H_2O)_{167}$ (2). Compound **2** crystallizes in triclinic space group $P\bar{1}$ and displays two crystallographically independent tetramers constructed by {Dy_{26}} clusters. Each asymmetric unit consists of 4 crystallographically independent $[Dy_{26}(\mu_3\text{-OH})_{20}(\mu_3\text{-O})_6(NO_3)_9I]^{36+}$ cores, 125 IN ligands, 19 OH anions, and 167 H_2O molecules. Four {Dy_{26}} cores possess identical compositions, which are also identical to that of the {Dy_{26}} core in **1**. However, one of these cores called (Dy_{26})-4, possesses a slightly different construction than that of **1**, mainly resulting from the coordination modes of NO_3^- ligands. In the structure of (Dy_{26})-4 core, eight NO_3^- ligands adopt coordination mode **I**, while the ninth one adopts coordination mode **II**.

All these {Dy_{26}} clusters in **2** also can be regarded as the assembly of five cubane-like {Dy_4} clusters and six additional Dy(III) centers, however, each of these {Dy_{26}} clusters has different composition. Thirty-one IN ligands coordinate to one core called {Dy_{26}}-1 through the carboxylate oxygen atoms and pyridyl nitrogen atom (Figure S4 in the Supporting Information). These 31 IN ligands can be divided into five classes: 5 with mode **III**, 2 with mode **IV**, 22 with mode **V**, 1 with mode **VII**, and 1 with mode **VIII**. Thirty-two IN ligands, which include four with mode **III**, five with **IV**, twenty-one with **V**, one with **VII**, and one with **VIII**, coordinate to another core entitled {Dy_{26}}-2 (Figure S5 in the Supporting Information). Additionally, 31 and 33 IN ligands coordinate to remaining two cores entitled {Dy_{26}}-3 and {Dy_{26}}-4, respectively. The linkage of {Dy_{26}}-1 and {Dy_{26}}-2 cores through IN linkers gives rise to an unusual tetramer with a rhombic shape (Figure 3b). The rhombus size is 35.13 × 34.24 Å. Moreover, the linkage of {Dy_{26}}-3 and {Dy_{26}}-4 cores through IN linkers generate another tetramer in the structure of **2**.

Compounds **1** and **2** have much in common: both contain the $[Dy_{26}(\mu_3\text{-OH})_{20}(\mu_3\text{-O})_6(NO_3)_9I]^{36+}$ cluster core motif in their crystal structures. This could be related to the fact that NO_3^- ligands with full coordination modes are incorporated into the cluster core backbones, thus expanding the cluster core surface and decreasing the positive charge, which leads to a large cluster with higher nuclearity. Despite the similarity among **1** and **2**, these clusters fulfill different functions in the construction of these tetramers. On the other hand, compounds **1** and **2** could not be obtained by the above reaction when AgI was replaced by other species containing iodine, which suggests that the slow release of iodine ions in AgI species plays an important role in the formation of cage-shaped {Dy_{26}} clusters. In the structures of **1** and **2**, iodine ions are incorporated into the cluster centers, which also indicates that iodine ions induce the formation of these large clusters through a template effect.[6c,18]

Conclusion

In conclusion, we have synthesized two novel lanthanide cluster compounds by introduction of NO_3^- ligands with trigonal planar geometry planted into the cluster core backbone through coordination bonds. Both compounds contain nanosized {Dy_{26}} clusters, which are the largest cage-shaped lanthanide clusters known. Moreover, compound **1** represents the first tetramer based on the linkage of two different types of high-nuclearity lanthanide clusters and IN ligands, and compound **2** is the first tetramer assembled by the {Dy_{26}} clusters and IN linkers. This strategy for the surface modification of cluster core backbones can be employed to design and synthesize nanosized lanthanide cluster-based materials.

Acknowledgment. This work was financially supported by the Program for New Century Excellent Talents in University (Grant 05-0278), the National Natural Science Foundation of China (Grant 20471012), and the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (Grant 200322).

Supporting Information Available: X-ray crystallographic file (CIF) for compounds **1** and **2**, IR spectra, TG curves, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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