Inorg. Chem. **2006**, *45*, 5162–5166

Inorganic Chemistry
Article

Cluster-Type Basic Lanthanide Iodides $[M_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (M = Nd, Eu, Tb, Dy)[†]

Anja-Verena Mudring,* Tudor Timofte, and Arash Babai

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, Köln 50939, Germany

Received July 25, 2005

$Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (Ln = Nd, Eu, Tb, Dy) compounds are obtained as the final hydrolysis products of lanthanide triiodides in an aqueous solution. Their X-ray crystal structure features a body-centered arrangement of oxygen-centered $\{Ln_6X_8\}^{8+}$ cluster cores: $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ [Pearson code oP156, orthorhombic, *Pnnm* (No. 58), $Z = 2$, $a = 1310.4(3)$ pm, $b = 1502.1(3)$ pm, $c = 1514.9(3)$ pm, 3384 reflections with $I_0 > 2\sigma(I_0)$, R1 = 0.0340, wR2 = 0.0764, GOF = 1.022, $T = 298(2)$ K], $[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ [Pearson code oP156, orthorhombic, *Pnnm* (No. 58), $Z = 2$, $a = 1306.6(2)$ pm, $b = 1498.15(19)$ pm, $c = 1499.41(18)$ pm, 4262 reflections with $I_0 > 2\sigma(I_0)$, R1 = 0.0540, wR2 = 0.0860, GOF = 0.910, $T = 298(2)$ K], $[Tb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ [Pearson code oP156, orthorhombic, *Pnnm* (No. 58), $Z = 2$, $a = 1296.34(5)$ pm, $b = 1486.13(7)$ pm, $c = 1491.88(6)$ pm, 4182 reflections with $I_0 > 2\sigma(I_0)$, R1 = 0.0395, wR2 = 0.0924, GOF = 1.000, $T = 298(2)$ K], and $[Dy_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ [Pearson code oP156, orthorhombic, *Pnnm* (No. 58), $Z = 2$, $a = 1296.34(5)$ pm, $b = 1486.13(7)$ pm, $c = 1491.88(6)$ pm, 3329 reflections with $I_0 > 2\sigma(I_0)$, R1 = 0.0389, wR2 = 0.0801, GOF = 0.992, $T = 298(2)$ K.

Introduction

Polynuclear metal−oxo and −hydroxo complexes are of interest not only because of their promising application as advanced materials (magnets, optical materials, catalysts[1]) but also because of their potential biological relevance. It is known that polynuclear lanthanide−hydroxo complexes are capable of catalyzing the hydrolytic cleavage of RNA and DNA.[2]

However, generally applicable synthetic procedures toward defined lanthanide oxo/hydroxo cluster compounds are scarce. Simple hydrolysis of lanthanide ions is commonly believed to be of limited synthetic quality because it leads to unpredictable, serendipitous, and ill-defined lanthanide hydroxides and oxo/hydroxides[3] as a result of the inherent properties of the lanthanide cations. The high charge and the polarizing power result in a high tendency to readily hydrolyze in aqueous solutions. Additionally, trivalent rare-earth ions being large cations show variable coordination numbers and geometries with small energy differences. Thus, it is generally difficult to control the oligomerization of rare-earth centers.[4] A common synthetic strategy toward higher polynuclear lanthanide and other metal clusters is to introduce auxiliary ligands such as carboxylates, polyketonates, polyamines, polyols, pyridonate, alkoxides, and α-amino acids[1,4] in the metal coordination sphere in order to control the advancement of hydrolysis (“ligand-controlled hydrolysis”) and prevent the disruption of the cluster architecture by additional water.

Here we show that cluster-type basic lanthanide iodides, $([Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_{12}$, can be easily obtained via direct hydrolysis of lanthanide iodides in the absence of any organic auxiliary ligands and strong bases because these compounds mark the end point of hydrolysis under ambient conditions.

Experimental Section

Synthesis. $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (1), $[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (2), $[Tb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (3), and $[Dy_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (4). For **1**,

---

[†] Dedicated to Prof. Dr. Josef Hahn on the occasion of his 65th birthday.

* To whom correspondence should be addressed. E-mail: a.mudring@uni-koeln.de.

(1) Zheng, Z. *Chem. Commun.* **2001**, 2521 and references cited therein. Zheng, Z. In *Inorganic Synthesis*; Shapley, J. R., Ed.; Wiley-Interscience: New York, 2004; p 184.

(2) Oh, S. J.; Song, K. H.; Whang, D.; Kim, K.; Yoon, T. H.; Moon, H.; Park, J. W. *Inorg. Chem.* **1996**, *35*, 3780.

(3) Cotton, S. A. *Lanthanides and Actinides*; Macmillan: London, 1991.

(4) Anwander, R. *Angew. Chem.* **1998**, *110*, 619; *Angew. Chem., Int. Ed.* **1998**, *37*, 599.

10.1021/ic051234s CCC: $33.50

Table 1. Crystal Data and Structure Refinement Parameters for $[M_6(\mu^6\text{-}O)(\mu^3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$

	1	**2**	**3**	**4**
empirical formula	$Nd_6I_8O_{41}H_{72}$	$Eu_6I_8O_{41}H_{72}$	$Tb_6I_8O_{41}H_{72}$	$Dy_6I_8O_{41}H_{72}$
temp, K	293(2)	293(2)	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pnnm* (No. 58)	*Pnnm* (No. 58)	*Pnnm* (No. 58)	*Pnnm* (No. 58)
unit cell dimens				
a, pm	1310.4(3)	1306.6(2)	1296.34(5)	1296.34(5)
b, pm	1502.1(3)	1498.15(19)	1486.13(7)	1486.13(7)
c, pm	1514.9(3)	1499.41(18)	1491.88(6)	1491.88(6)
$\alpha = \beta = \gamma$, deg	90	90	90	90
V, Å^3	2981.9(10)	2935.0(7)	2874.2(2)	2874.2(2)
Z	2	2	2	2
density (calcd), mg/m^3	2.906	3.005	3.117	3.058
abs coeff, mm^{-1}	9.351	10.604	11.664	12.078
F(000)	2368	2404	2428	2296
cryst size, mm^3	0.1 × 0.2 × 0.3	0.1 × 0.2 × 0.3	0.1 × 0.2 × 0.3	0.1 × 0.2 × 0.3
θ range for data collection, deg	1.91−26.99	1.92−29.63	1.93−29.61	1.93−27.27
index ranges	$-16 \leq h \leq 16$	$-18 \leq h \leq 18$	$-17 \leq h \leq 17$	$-16 \leq h \leq 16$
	$-19 \leq k \leq 19$	$-20 \leq k \leq 20$	$-20 \leq k \leq 20$	$-18 \leq k \leq 19$
	$-19 \leq l \leq 19$	$-20 \leq l \leq 20$	$-20 \leq l \leq 20$	$-19 \leq l \leq 19$
reflns collected	37 273	40 668	46 926	41 933
independent reflns	3384 [*R*(int) = 0.0590]	4262 [*R*(int) = 0.1766]	4182 [*R*(int) = 0.1255]	3329 [*R*(int) = 0.0881]
completeness to $\theta = 29.61°$, %	100.0	99.3	99.5	99.4
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	3384/0/149	4262/0/150	4182/0/149	3329/0/149
GOF on F^2	1.022	0.910	1.000	0.992
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0340, wR2 = 0.0764	R1 = 0.0540, wR2 = 0.0860	R1 = 0.0395, wR2 = 0.0924	R1 = 0.0389, wR2 = 0.0801
R indices (all data)	R1 = 0.0447, wR2 = 0.0794	R1 = 0.1060, wR2 = 0.0998	R1 = 0.0571, wR2 = 0.098	R1 = 0.0644, wR2 = 0.0866
largest diff peak and hole, e/Å^3	0.568 and −0.733	0.194 and −0.216	0.359 and −0.239	0.319 and −0.218
CSD no.	391285	415343	415344	415622

1 g (2.13 mmol) of neodymium carbonate [($Nd_2(CO_3)_3$), 99.9%, Aldrich], for **2**, 1 g (2.84 mmol) of europium oxide [(Eu_2O_3), >99%, Merck], for **3**, 1 g (1.33 mmol) of terbium oxide [(Tb_4O_7), 99.9%, Reacton], and for **4**, 1 g (2.68 mmol) of dysprosium oxide [(Dy_2O_3), 99.9%, Reacton] were dissolved in 4.5 mL of hydroiodic acid (twice distilled before use, 57 wt %, aqueous solution, unstabilized, Acros Organics). The respective solution was heated under continuous stirring to 45−50 °C and held at this temperature for approximately 40 min. The solution was then allowed to slowly cool to room temperature. After exposure of the solution for a prolonged period of time (∼6−8 weeks) to a normal atmosphere at room temperature, pale-pink crystals of compound **1**, yellow, polyhedric crystals of compound **2**, transparent, prismatic crystals of compound **3**, and pale-yellow, prismatic crystals of compound **4** grew from the solution. By that time, the pH of the solution had reached a value of 7−8.

Crystals suitable for single-crystal X-ray diffraction studies were selected from the bulk samples under a microscope sealed in thin-walled glass capillaries of 0.3-mm outer diameter and were checked by Laue photographs for their quality. The best crystals of the respective compounds **1**−**4** were used to collect a complete intensity data set with the aid of a single-crystal X-ray diffractometer (Stoe IPDS-II image plate diffraction system) at room temperature.

Average yields: ∼60%. IR (cm^{-1}): $[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$, 3426.5 (s), 2923.74 (w), 2853.34 (w), 1629.3 (m), 1444.51 (w), 1384.2 (m), 1326.86 (w), 1114.72 (w), 1043.36 (w), 767.57 (w), 541.93 (w), 472.5 (w). $[Tb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$, 3421.8 (s), 1621.4 (m), 1457.4 (w), 1384.3 (m), 1330. 7 (w), 1043.4 (w), 772.6 (w), 490.5 (w).

Further analytical data are available as Supporting Information.

X-ray Crystal Structure Determination. All data were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 293(2) K. Analysis of the reflection conditions led to the possible space groups *Pnn*2 (No. 34) and *Pnnm* (No. 58). Structure solution[5] and refinement[6] succeeded in the space group *Pnnm* (No. 58). Crystal structure solution of compounds **1**, **3**, and **4** in this space group by direct methods using *SHELXS-97* yielded the heavy-atom positions. Subsequent difference Fourier analysis and least-squares refinement allowed localization of the oxygen atom positions. The crystal of compound **2** turned out to be a merohedric twin. Crystals of **2**−**5** showed a strong tendency to twin because of the comparable lengths of the crystallographic *b* and *c* axes. Refinement as a merohedric twin led to satisfactory results. Crystal data and structural refinement parameters of the four structures are summarized in Tables 1−5. Data reduction was carried out with the program package *X-Red*[7] and numerical absorption correction with the program *X-Shape*.[8] For crystal structure drawings, the program *Diamond* was employed.[9] Further details of the structure refinement may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, crysdata@FIZ-Karlsruhe.de, referring to

---

(5) Sheldrick, W. S. *SHELXS-97*; Universität Göttingen: Göttingen, Germany, 1997.

(6) Sheldrick, W. S. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.

(7) *X-Red*; Stoe & Cie: Darmstadt, Germany, 2002.

(8) *X-Shape*; Stoe & Cie: Darmstadt, Germany, 2002.

(9) *Diamond*, version 2.1e; Crystal Impact GbR: Bonn, Germany, 1996−2001.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]	occupancy
Nd1	5000	5000	3280(1)	45(1)	1
Nd2	4584(1)	6705(1)	5000	44(1)	1
Nd3	6966(1)	5359(1)	5000	44(1)	1
I1	5000	0	−3509(1)	105(1)	1
I2	2856(1)	2178(1)	−2616(1)	85(1)	1
I3	4945(1)	3211(1)	0	82(1)	1
O1	5000	5000	5000	44(2)	1
O2	6403(3)	4200(2)	3979(3)	46(1)	1
O3	5910(3)	6213(2)	6010(3)	45(1)	1
O4	3427(6)	4685(6)	2235(5)	109(2)	1
O5	5292(6)	3718(5)	2242(4)	94(2)	1
O6	4337(4)	7723(3)	6352(4)	75(1)	1
O7	5831(6)	8056(5)	5000	71(2)	1
O8	2810(6)	7415(6)	5000	80(2)	1
O9	8518(6)	4336(6)	5000	78(2)	1
O10	8072(4)	5535(4)	6372(4)	75(1)	1
O11	7780(7)	6925(6)	5000	101(3)	1
O12	90(4)	6162(5)	6356(5)	87(2)	1
O13	2333(13)	4227(10)	656(12)	107(4)	0.5
O14	2871(14)	5444(11)	738(11)	114(5)	0.5

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **2**

	x	*y*	*z*	*U*(eq)[a]	occupancy
Eu1	5000	5000	3301(1)	52(1)	1
Eu2	4596(1)	6685(1)	5000	51(1)	1
Eu3	6947(1)	5345(1)	5000	51(1)	1
I1	5000	0	−3515(2)	108(1)	1
I2	2844(1)	2179(1)	−2623(1)	90(1)	1
I3	4952(2)	3232(1)	0	90(1)	1
O1	5000	5000	5000	60(5)	1
O2	6391(7)	4207(6)	3982(7)	56(2)	1
O3	5904(8)	6197(7)	6013(6)	56(2)	1
O4	3423(11)	4701(13)	2243(9)	111(6)	1
O5	5276(13)	3736(10)	2272(9)	100(5)	1
O6	4357(10)	7712(7)	6350(8)	75(3)	1
O7	5841(12)	8015(9)	5000	67(4)	1
O8	2874(13)	7396(11)	5000	79(5)	1
O9	8457(12)	4288(13)	5000	78(5)	1
O10	8074(8)	5523(9)	6354(8)	79(3)	1
O11	7797(14)	6892(14)	5000	95(6)	1
O12	94(11)	6204(10)	6356(5)	91(4)	1
O13	2340(30)	4185(18)	626(18)	95(8)	0.5
O14	2880(30)	5450(30)	710(20)	127(12)	0.5

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **3**

	x	*y*	*z*	*U*(eq)[a]	occupancy
Tb1	5000	5000	3321(1)	57(1)	1
Tb2	4603(1)	6674(1)	5000	56(1)	1
Tb3	6937(1)	5343(1)	5000	56(1)	1
I1	5000	0	−3506(1)	117(1)	1
I2	2839(1)	2184(1)	−2622(1)	94(1)	1
I3	4939(1)	3233(1)	0	93(1)	1
O1	5000	5000	5000	55(2)	1
O2	6375(4)	4208(3)	3988(3)	59(1)	1
O3	5904(4)	6191(3)	5997(3)	60(1)	1
O4	3430(9)	4692(9)	2266(6)	130(3)	1
O5	5256(7)	3770(6)	2275(5)	103(2)	1
O6	4370(6)	7678(4)	6341(5)	84(2)	1
O7	5829(8)	8008(6)	5000	85(2)	1
O8	2879(8)	7383(7)	5000	87(2)	1
O9	8437(8)	4283(7)	5000	87(2)	1
O10	8043(5)	5518(5)	6343(5)	86(2)	1
O11	7774(8)	6870(7)	5000	99(3)	1
O12	71(6)	6160(6)	6330(5)	97(2)	1
O13	2681(19)	9191(12)	5659(16)	131(7)	0.5
O14	2897(19)	5445(14)	743(14)	126(6)	0.5

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **4**

	x	*y*	*z*	*U*(eq)[a]	occupancy
Dy1	5000	5000	3322(1)	63(1)	1
Dy2	4609(1)	6668(1)	5000	61(1)	1
Dy3	6938(1)	5339(1)	5000	62(1)	1
I1	5000	0	−3501(1)	134(1)	1
I2	2827(1)	2187(1)	−2622(1)	103(1)	1
I3	4929(1)	3239(1)	0	105(1)	1
O1	5000	5000	5000	62(2)	1
O2	6374(4)	4208(4)	3987(4)	62(1)	1
O3	5909(4)	6187(4)	6002(4)	61(1)	1
O4	3443(11)	4719(10)	2261(7)	162(5)	1
O5	5265(9)	3788(8)	2274(6)	125(3)	1
O6	4388(6)	7672(5)	6329(6)	93(2)	1
O7	5819(9)	7996(7)	5000	95(3)	1
O8	2913(9)	7398(8)	5000	96(3)	1
O9	8446(8)	4310(9)	5000	99(3)	1
O10	8038(5)	5516(6)	6337(5)	92(2)	1
O11	7782(9)	6862(9)	5000	111(4)	1
O12	75(6)	6169(7)	6323(6)	108(2)	1
O13	2310(20)	4210(16)	620(20)	158(9)	0.5
O14	2940(20)	5419(19)	732(18)	154(8)	0.5

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

CSD Nos. 391285 for **1**, 415343 for **2**, 415344 for **3**, and 415622 for **4**, the authors, and the journal citations.

Results and Discussion

$[\mathrm{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mathrm{H_2O})_{24}]\mathrm{I}_8(\mathrm{H_2O})_8$ (Ln = Nd, Eu, Tb, Dy) compounds crystallize isotypically in the orthorhombic space group *Pnnm* (No. 58) with two formula units in the unit cell. The structure of these basic lanthanide iodides is characterized by a (slightly distorted) Ln^{3+} octahedron, which is centered by an oxygen anion, O^{2-} (Figure 1). Above each face of the $\{\mathrm{OLn}_6\}$ octahedron is located a hydroxide anion, OH^-. The hydroxide anions themselves, thus, build up a (slightly distorted) cube, the inverse platonic polyhedron of an octahedron. Each lanthanide cation carries four additional water molecules in terminal positions. Altogether, for the lanthanide, a 4 + 4 + 1 coordination of Ln^{3+} by oxygen is achieved.

The $[\mathrm{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mathrm{H_2O})_{24}]^{8+}$ cluster units arrange themselves in a body-centered fashion, connected three-dimensionally by iodine anions (I2) that are located above the octahedral faces of two neighboring units (Figure 2). Additional iodine anions are terminally shared between two (I1) and three (I3) different cluster units. The crystal structure is completed by the remaining crystal water molecules (O11−O14). Because of the oxygen position, O13 and O14 are just half-occupied. Erroneously, $[\mathrm{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mathrm{H_2O})_{24}]\mathrm{I}_8(\mathrm{H_2O})_8$ was been described in a first communication as $[\mathrm{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\mathrm{H_2O})_{24}]\mathrm{I}_{12}\cdot 12\mathrm{H_2O}$.[10]

---

(10) Mudring, A.-V.; Babai, A. *Z. Anorg. Allg. Chem.* **2005**, *631*, 261.

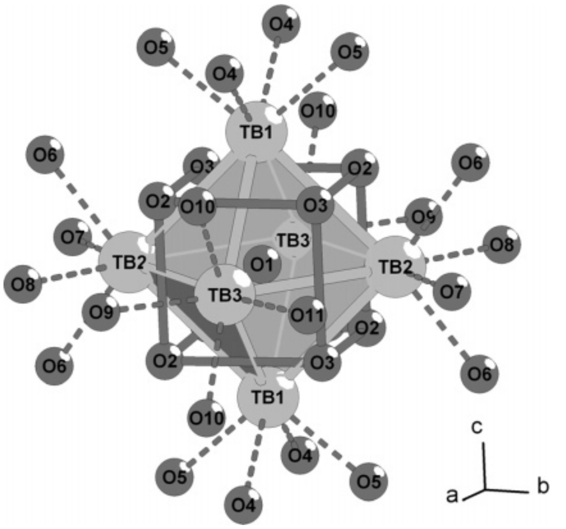

Figure 1. $[Tb_6(\mu^6\text{-}O)(\mu^3\text{-}OH)_8(H_2O)_{24}]^{8+}$ cluster unit.

The observed interatomic distances in $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ (Ln = Nd, Eu, Tb, Dy) are in agreement with the contraction of ionic radii along the row of trivalent lanthanide cations.[11] Not only do the mean metal−metal distances decrease from Nd to Dy [*d*(Nd−Nd) = 370.09(7) pm, *d*(Eu−Eu) = 363.7(1) pm, *d*(Tb−Tb) = 358.36(5) pm, and *d*(Dy−Dy) = 357.14(8) pm], but the metal−oxygen distances do also (cf. Tables 6−9).

Although the $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]^{8+}$ cluster unit has been reported previously for basic perchlorates as in $[Nd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}](ClO_4)_8(H_2O)_8$[12] and $[Gd_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}](ClO_4)_8(H_2O)_8$,[12,13] compounds **2**−**4** are the first examples of europium, terbium, and dysprosium compounds with this cluster unit. It is worth noting that $[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ is an example of a compound where Eu^{3+} exists in the presence of iodide and is not reduced to Eu^{2+}.[14]

It seems that for the formation of the $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]^{8+}$ cluster unit the oxo anion works as a template to induce the self-assembly of lanthanide ions. The structure-directing effect of a "central spherical negative charge density" such as for product formation has already been assumed in another context.[4] pH conditions exert a crucial influence on the generation of the central oxo anion. In a highly acidic medium, the reaction of lanthanide oxides with HI results in the formation of lanthanide iodide hydrates, e.g., $NdI_3{\cdot}9H_2O$.[15] If one allows the pH value to decrease by evaporation of HI, the formation of $[Ln_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_8$ is observed as the final product of hydrolysis.

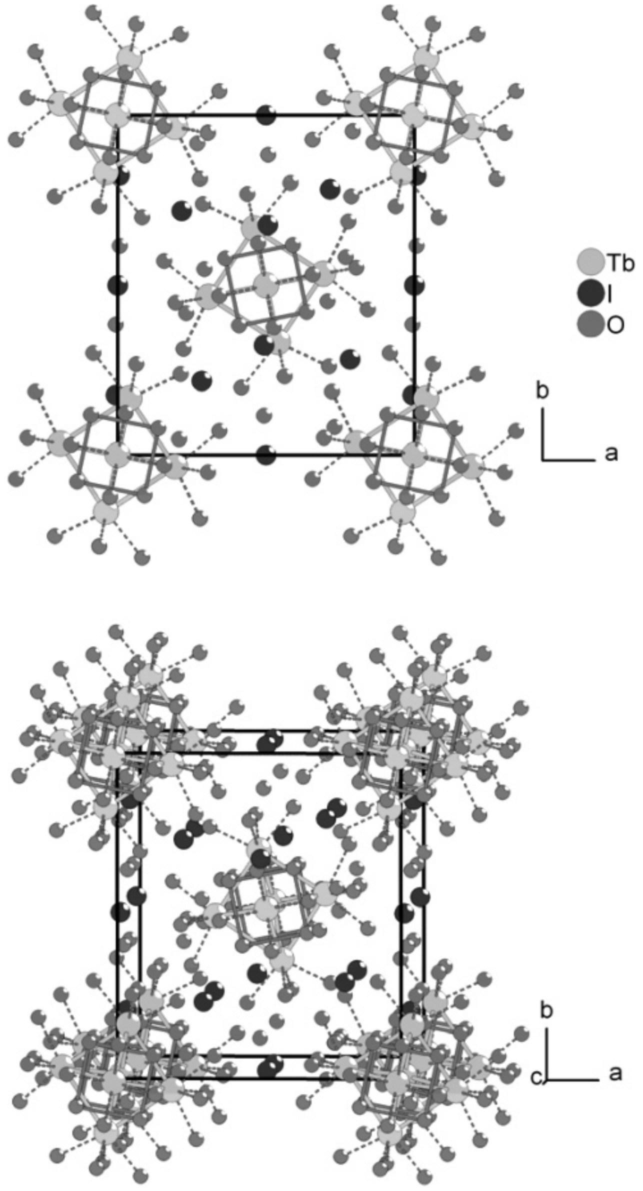

Figure 2. Crystal structure of $[Tb_6(\mu^6\text{-}O)(\mu^3\text{-}OH)_8(H_2O)_{24}]I_8(H_2O)_{12}$: (a) projection along [001]; (b) perspective view.

Table 6. Selected Bond Lengths in pm for **1**

		CN			CN
Nd1−O3	242.9(4)	2	Nd3−O3	242.9(4)	2
Nd1−O2	243.8(4)	2	Nd3−O2	244.4(4)	2
Nd1−O5	251.6(6)	2	Nd3−O10	254.6(5)	2
Nd1−O1	260.52(7)	1	Nd3−O9	254.8(7)	1
Nd1−O4	264.1(7)	2	Nd3−O11	258.3(8)	1
			Nd3−O1	263.25(6)	1
Nd2−O3	243.0(4)	2			
Nd2−O2	243.1(4)	2	Nd1−Nd2	369.32(7)	2
Nd2−O8	255.8(7)	1	Nd1−Nd3	370.36(7)	2
Nd2−O6	257.6(5)	2	Nd2−Nd3	370.59(8)	2
Nd2−O7	260.6(7)	1			
Nd2−O1	261.79(6)	1			

---

(11) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr. B* **1969**, *25*, 925. (b) Shannon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751. (c) Meyer, G.; Linzmeier, P. *Rev. Chim. Miner.* **1977**, *14*, 52.

(12) Zhang, D.-S.; Ma, B.-Q.; Jin, T.-Z.; Gao, S.; Yan, Ch.-H.; Mak, T. C. W. *New J. Chem.* **2000**, *24*, 61.

(13) Wang, R.; Carducci, M. D.; Zheng, Z. *Inorg. Chem.* **2000**, *39*, 1836−1837.

(14) To our knowledge (ICSD), the only other europium(III) iodide compounds are EuIO (Baernighausen, H. *J. Prakt. Chem.* **1961**, *14*, 313) and Bi_2EuIO_4 (Schmidt, M.; Oppermann, H.; Hennig, C.; Henn, R. W.; Gmelin, E.; Soeger, N.; Binnewies, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 125).

(15) Timofte, T.; Babai, A.; Meyer, G.; Mudring, A.-V. *Acta Crystallogr.* **2005**, *E16*, i87.

Table 7. Selected Bond Lengths in pm for **2**

		CN			CN
Eu1−O3	238.2(10)	2	Eu3−O3	240.7(10)	2
Eu1−O2	239.9(9)	2	Eu3−O2	240.2(10)	2
Eu1−O5	247.0(14)	2	Eu3−O10	252.2(12)	2
Eu1−O1	254.71(11)	1	Eu3−O9	253.0(16)	1
Eu1−O4	263.9(12)	2	Eu3−O11	257(2)	1
			Eu3−O1	259.64(11)	1
Eu2−O3	240.0(11)	2			
Eu2−O2	240.4(10)	2	Eu1−Eu2	362.49(9)	2
Eu2−O8	248.9(17)	1	Eu1−Eu3	363.72(11)	2
Eu2−O6	256.1(11)	2	Eu2−Eu3	364.94(15)	2
Eu2−O7	257.2(14)	1			
Eu2−O1	257.93(11)	1			

Table 8. Selected Bond Lengths in pm for **3**

		CN			CN
Tb1−O3	235.3(5)	2	Tb3−O3	236.5(5)	2
Tb1−O2	235.6(5)	2	Tb3−O2	237.9(5)	2
Tb1−O5	242.7(7)	2	Tb3−O10	247.8(6)	2
Tb1−O1	250.43(4)	1	Tb3−O9	250.2(9)	1
Tb1−O4	261.3(10)	2	Tb3−O11	251.6(9)	1
			Tb3−O1	256.23(4)	1
Tb2−O3	236.0(5)	2			
Tb2−O2	236.8(5)	2	Tb1−Tb2	356.69(4)	2
Tb2−O8	247.1(10)	1	Tb1−Tb3	358.29(4)	2
Tb2−O6	251.4(6)	2	Tb2−Tb3	360.09(6)	2
Tb2−O7	254.1(9)	1			
Tb2−O1	253.99(4)	1			

Table 9. Selected Bond Lengths in pm for **4**

		CN			CN
Dy1−O3	234.3(6)	2	Dy3−O3	236.7(5)	2
Dy1−O2	234.7(5)	2	Dy3−O2	237.5(6)	2
Dy1−O5	241.9(9)	2	Dy3−O10	246.6(7)	2
Dy1−O1	248.79(6)	1	Dy3−O9	248.3(11)	1
Dy1−O4	260.9(12)	2	Dy3−O11	251.5(12)	1
			Dy3−O1	256.19(5)	1
Dy2−O3	236.3(5)	2			
Dy2−O2	236.7(6)	2	Dy1−Dy2	354.88(6)	2
Dy2−O8	245.2(11)	1	Dy1−Dy3	357.11(6)	2
Dy2−O6	249.7(8)	2	Dy2−Dy3	359.43(8)	2
Dy2−O7	252.0(11)	1			
Dy2−O1	253.07(6)	1			

The existence of $\{[(DMF)_{16}Yb_6(\mu_6\text{-O})(\mu_3\text{-OH})_8)(\mu\text{-NC})\text{-}Pd_2(\mu\text{-CN})(CN_2)_{20}]\ (ClO_4)_6\cdot4(H_2O)_{12}$[16] (where DMF = *N*,*N*-dimethylformamide) shows not only that a further derivatization of the $[Ln_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(H_2O)_{24}]^{8+}$ cluster unit by exchange of the water ligands is feasible but also that a connection of the rare-earth clusters to other metal centers should be possible. This may potentially open up access to new interesting materials such as open-framework structures with the $[Ln_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(H_2O)_{24}]^{8+}$ cluster units as building blocks or molecular magnets (especially when coupling a transition metal to a rare earth with a high magnetic moment, although the dipolar exchange of even only ytterbium centers was currently observed at low temperatures[17]). Preliminary solvation studies show that the cluster compounds readily dissolve in DMF in contrast to other conventional organic solvents such as tetrahydrofuran or acetonitrile.

Acknowledgment. The Fonds der Chemischen Industrie and the Deutsche Forschunsgemeinschaft (SPP 1166) are acknowledged for financial support. T.T.'s research stay is funded by the SOKRATES-EU program. Prof. Dr. Gerd Meyer is gratefully acknowledged for his continuous support.

Supporting Information Available: X-ray crystallographic data for **1**−**4** (CIF format) and IR spectra, powder patterns, and the results of EDX analyses for $[M_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(H_2O)_{24}]I_8\cdot(H_2O)_8$ (M = Eu, Tb). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051234S

---

(16) Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 5410.

(17) Fang, X.; Anderson, T. M.; Benelli, C.; Craig, C. L. *Chem.*—*Eur. J.* **2005**, *11*, 712.