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Novel Mixed-Metal Alkoxide Clusters of Lanthanide and Sodium: Synthesis and Extremely Active Catalysts for the Polymerization of ϵ-Caprolactone and Trimethylene Carbonate

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Novel mixed-metal alkoxide clusters of lanthanide and sodium $[Ln_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$, which were synthesized in reproducible high yields and structurally characterized, were found to be extremely active catalysts for the ring-opening polymerization of ϵ-caprolactone and trimethylene carbonate.

Inorganic clusters continue to attract considerable attention because they are not only the precursors for the sol−gel technology[1] but also useful tools for understanding the size-dependent physical properties of electronic materials.[2] Alkoxide ligands, because their electronic and steric environment can easily be modified, are ideal for cluster design/stabilization involving the large oxophilic lanthanide metal ions.[3] Numerous structurally characterized lanthanide alkoxide clusters have been reported by chloride-,[4a−d] oxo-,[4c,5,6] and hydroxo[4d,7]-driven formation. However, the rational synthesis of clusters is still a steady challenge because the chemistry of alkoxide clusters has proven to be complicated, with the reaction products depending not only upon the stoichiometries of the reagents[4] but also upon those of the central metal ions.[4b,7b]

The formation of mixed-metal clusters with unique chemical or physical properties might be one of the most interesting topics in lanthanide alkoxide cluster chemistry because these clusters are of interest for exploring lanthanide-doped materials and efficient bimetallic catalysts. Although a variety of lanthanide−aluminum clusters have been reported for these purposes,[9] the study of the synthesis and catalytic behavior

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of mixed-metal alkoxide clusters of lanthanide and alkali metals is relatively limited.[3e,4c−e,6a,8,10]

Here we report the synthesis of a novel mixed-metal alkoxide cluster of lanthanide and sodium $[Ln_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$ using hydroxo-driven formation. The new synthetic strategy presented here is to use a definite amount of sodium hydroxide as the hydroxo driving force. The method has proven to provide the products in reproducible high yields and to be available to the lanthanide metals from light to heavy. Moreover, the clusters were found to be extremely active catalysts for the polymerization of ϵ-caprolactone (ϵ-CL) and trimethylene carbonate (TMC).

The metathesis reaction of anhydrous $NdCl_3$ with 3 equiv of $Na(OCH_2CH_2NMe_2)$ in tetrahydrofuran (THF) at room temperature gave the cluster $[Nd_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$ (**1**) as blue crystals in less than 2% yield, which was characterized by conventional techniques and single-crystal X-ray diffraction (Scheme 1).

Scheme 1

$$3NaOCH_2CH_2NMe_2 + NdCl_3 \rightarrow [Nd_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$$

$$\text{Yield} = 2\%$$

The hydroxo groups in the product are likely to be introduced as a contaminant in the $Na(OCH_2CH_2NMe_2)$ reagent used. Therefore, the shortage of both NaOH and $Na(OCH_2CH_2NMe_2)$ might be considered to be the reason for the low yield. Really, the yield of cluster **1** can be improved considerably (from 2% to 73%; yield based on neodymium) by adding 1 equiv of NaOH and an additional 3 equiv of $Na(OCH_2CH_2NMe_2)$ to the reaction mixture (Scheme 2). To testify to the validity of this approach, the analogous reactions of $LnCl_3$ with 6 equiv of $Na(OCH_2CH_2NMe_2)$ and 1 equiv of NaOH were conducted, and the corresponding lanthanide−sodium clusters $[Ln_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$ [Ln = Sm (**2**), Y (**3**), Ho (**4**)] were successfully isolated in high yields (Scheme 2).

Scheme 2

$$6NaOCH_2CH_2NMe_2 + LnCl_3 + NaOH \rightarrow 0.5[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2] + 3NaCl$$

Ln = Nd (**1**; 73%), Sm (**2**; 79%), Y (**3**;76%), Ho (**4**; 65%)

Single-crystal X-ray analyses for **1**, **2**, and **4** established that all clusters have the same structural motif. Figure 1 shows the molecular structures of **1**, **2**, and **4**, and the figure caption gives the list of significant bond lengths and angles. As shown in Figure 1, each cluster contains 2 lanthanide metals, 8 sodium metals, and 12 $OCH_2CH_2NMe_2$ groups in addition to 2 OH groups. All of the metals are connected together by two μ_6-OH groups. A double-cubane framework as a central core is constructed by two lanthanide ions, four sodium ions, and six oxygen atoms with one face of a $Ln_2Na_2O_4$ cubane cluster capped by an additional Na_2O_2 layer. The central core, $Ln_2Na_4O_6$, has been capped on two opposite sides by Na_2O_3 units. Each lanthanide ion is coordinated to two μ_3-$OCH_2CH_2NMe_2$ groups, two μ_2-$OCH_2CH_2NMe_2$ groups, and two μ_6-OH groups, forming a distorted octahedron. Such persistence suggested that the structure framework here is particularly stable.

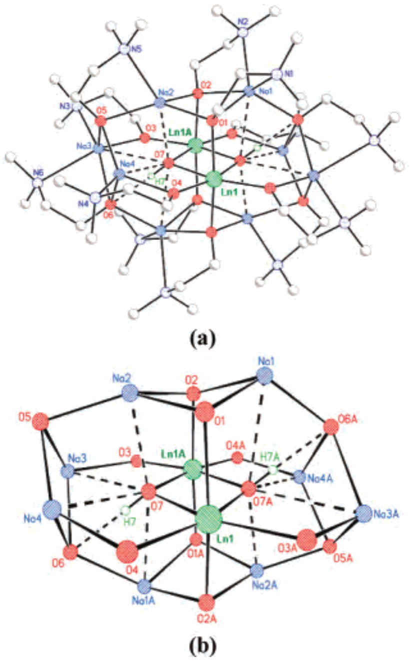

Figure 1. (a) Molecular structures of **1**, **2**, and **4**. (b) ORTEP diagram of **1**, **2**, and **4** with all of the $CH_2CH_2NMe_2$ groups omitted for clarity (atomic displacement parameters set at the 30% level). Selected bond distances (Å) and angles (deg): **1**, Nd1−O4 2.2779(18), Nd1−O3A 2.2935(19), Nd1−O2A 2.3635(18), Nd1−O1 2.3717(18), O4−Nd1−O3A 116.23(7), O2A−Nd1−O1 163.62(6); **2**, Sm1−O4 2.240(3), Sm1−O3A 2.264(3), Sm1−O2A 2.326(3), Sm1−O1 2.339(3), O4−Sm1−O3A 115.05(13), O2A−Sm1−O1 165.04(11); **4**, Ho1−O4 2.181(3), Ho1−O3A 2.198(3), Ho1−O2A 2.274(3), Ho1−O1 2.282(3), O4−Ho1−O3A 110.46(13), O2A−Ho1−O1 167.96(11).

The average bond lengths of Ln-μ_2-$OCH_2CH_2NMe_2$ [2.286(18) Å for **1**, 2.252(3) Å for **2**, and 2.190(3) Å for **4**] and Ln-μ_3-$OCH_2CH_2NMe_2$ [2.368(18) Å for **1**, 2.333(3) Å for **2**, and 2.278(3) Å for **4**] are comparable with each other when the differences in the ionic radii among Nd, Sm, and Ho are considered. The 0.08 Å larger for Ln-μ_3-$OCH_2CH_2NMe_2$ in comparison with that of Ln-μ_2-$OCH_2CH_2NMe_2$ is reasonable, and it is also observed in other alkoxide clusters.[5] The coordination environment around sodium ions can be divided into two classes. Na(1), Na(1)A, Na(3), and Na(3)A are six-coordinated in a distorted octahedron with four oxygen atoms and two nitrogen atoms, while Na(2), Na(2)A, Na(4), and Na(4)A are five-coordinated in a distorted trigonal bipyramid with four oxygen atoms and one nitrogen atom.

The catalytic activity of these clusters for the polymerization of ϵ-CL and TMC was examined, and the preliminary results are summarized in Table 1.

All of the clusters are extremely active catalysts. Taking cluster **1** as an example, the polymerization proceeded rapidly and was completed in less than 1 min at 20 °C even when 15 000 equiv of ϵ-CL was charged. The activity of **1** reaches as high as 1.03×10^5 kg/mol·h. To our best knowledge,

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Table 1. Polymerization of ϵ-CL and TMC Initiated by **1**−**4**[a]

entry	init	[M]/[I][b] (mole ratio)	conv[c] (%)	M_n ($\times 10^4$)	PDI[d]	activity (kg/mol·h)
1	**1**	8000	100	8.1	1.47	5.47×10^4
2	**1**	10000	100	8.5	1.52	6.84×10^4
3	**1**	15000	100	9.0	1.58	1.03×10^5
4[e]	**1**	8000	20	2.1	1.77	
5[f]	**1**	10 000 + 10 000	100	17.9	1.42	
6	**2**	8000	77	3.1	1.56	4.21×10^4
7	**2**	6000	100	4.0	1.61	
8	**3**	6000	18			
9	**3**	3000	100	4.8	1.57	2.05×10^4
10	**4**	3000	83	4.7	1.55	1.70×10^4
11[g]	NaOR	200	0			
12[g]	$Nd(OR)_3$	1500	0			
13[h]	**1**	6000	96	3.5	1.74	3.53×10^4
14[h]	**1**	8000	94	4.4	1.79	4.61×10^4
15[i]	**1**	6000	62	2.6	2.04	

[a] Conditions: [I] = 0.01 mol/L, toluene as the solvent, 1 min, 20 °C. [b] [M]/[I] (mole ratio): number of moles of monomer/number of moles of cluster ([I] represents [cluster]). [c] Conv %: weight of polymer obtained/weight of monomer used. [d] Measured by GPC calibrated with standard polystyrene samples. [e] THF as the solvent. [f] Polymerization of 10 000 equiv of ϵ-CL in toluene at 20 °C for 1 min followed by the addition of 10 000 equiv of ϵ-CL for another 1 min. [g] Time = 60 min, OR = $OCH_2CH_2NMe_2$. [h] Conditions: monomer = TMC, [I] = 0.01 mol/L, toluene as the solvent, time = 1 min, temperature = 20 °C, [TMC] = 1 mol/L. [i] THF as the solvent.

this is the highest activity for the polymerization of ϵ-CL ever found in the literature.[11] This is in striking contrast with the reaction of either $Na(OCH_2CH_2NMe_2)$ or $Nd(OCH_2CH_2NMe_2)_3$. In both cases, no reactions were observed under the same conditions (Table 1, entries 11 and 12), although $Y(OCH_2CH_2NMe_2)_3$ was reported to be an efficient initiator for this polymerization.[12] All of the gel permeation chromatography (GPC) curves of the resulting polymers are unimodal with relatively narrow molecular weight distributions (M_w/M_n around 1.5), although the molecular weights of the resulting polymers are lower than those expected from the monomer-to-cluster ratio, suggesting that transfer reactions may take place. The results clearly indicate that the heterometallic cluster was really used as a single-component catalyst here. The polymerization system was still active even after complete consumption of the substrate. For example, cluster **1** produced a polymer in 100% yield within 1 min when the second 10 000 equiv of ϵ-CL was added to a completed polymerization solution of ϵ-CL (10 000 equiv) (Table 1, entries 2 and 5). The molecular weight of the polymer obtained was about twice that obtained from the initial polymerization solution, and the molecular weight distribution remained almost unchanged (Figure 2). Moreover, the activity of the clusters depended profoundly on lanthanide metals, **4** < **3** < **2** < **1** (Table 1). Such an "ionic radius effect" on the catalytic activity was also observed previously in the lanthanide-catalyzed ϵ-CL polymerization.[13]

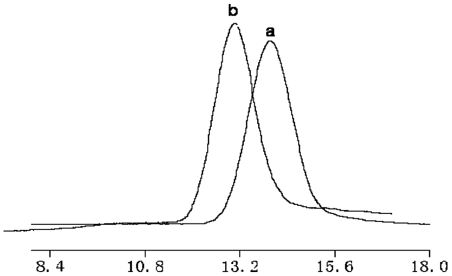

Figure 2. GPC curves of PCL (a) before and (b) after chain extension: (a) [M]/[I] = 10 000; (b) [M]/[I] = 10 000 + 10 000.

A strong solvent dependence of the polymerization was also observed. Both the yield and the molecular weight of the resulting polymer in toluene are much higher than those obtained in THF (Table 1, runs 1 and 4). In addition, cluster **1** is also an extremely active catalyst for the ring-opening polymerization of TMC. Almost complete conversion of the monomer into PTMC was achieved within 1 min at 20 °C for a monomer-to-cluster ratio of up to 8000. The effect of the solvent on the polymerization is the same as that found in the case of ϵ-CL; the polymerization in toluene is better than that in THF for the polymer yield and the molecular weight of the resulting polymer (Table 1, entries 13 and 15). Such a high activity for the mixed-metal cluster may reasonably be attributed to the cooperation of lanthanide and sodium metals resulting from the coordination of monomer to both metals concomitantly. In order to elucidate the polymerization mechanism, an oligomer of ϵ-CL was produced by the oligomerization of ϵ-CL with a [ϵ-CL]/[cluster] of 30 and terminated by isopropyl alcohol. The ^1H NMR spectroscopy of the oligomer revealed the presence of an end group of $OCH_2CH_2NMe_2$ at 2.36, 2.92, and 4.18 ppm, which indicates that the acyl−oxygen bond cleavage and the coordination−insertion mechanism should be supported. This result, together with the dependence of activity on the lanthanide metal, provides support for the suggestion that Ln−OR bonds may be the active species.

In summary, some novel mixed-metal alkoxide clusters of lanthanide and sodium were synthesized in reproducible high yields by a new synthetic strategy, which is available to the lanthanide metals from light to heavy. These mixed-metal clusters were found to be extremely active single-component catalysts for the ring-opening polymerization of ϵ-CL and TMC. These results indicated that the mixed-metal clusters might have great potential in the homogeneous catalysis as single-component catalysts.

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Supporting Information Available: X-ray crystallographic data for **1**, **2**, and **4** in CIF format and detailed experimental procedures for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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