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Note

Synthesis and molecular structure of a tetrameric neodymium-silsesquioxane cage complex: {[(*i*-C_4H_9)$_7$(Si_7O_{12}) Nd]$_4$NaCl}

Guangming Wu [a], Yaofeng Chen [b], Duan-Jun Xu [c], Jia-Chu Liu [d], Weilin Sun [a,*], Zhiquan Shen [a,*]

[a] *Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China*
[c] *Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China*
[d] *Technology Center of Equistar/Lyondell Chemicals LP, Cincinnati, OH 45249, USA*

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ABSTRACT

A new tetrameric neodymium-silsesquioxane cage complex {[(*i*-C_4H_9)$_7$(Si_7O_{12})Nd]$_4$NaCl} (**1**) was prepared by the reaction of $NdCl_3$ with *i*-PrONa, and subsequent treatment with trisilanol [(*i*-C_4H_9)$_7$(Si_7O_9)(OH)$_3$] in toluene. The molecular structure of the complex was determined by single crystal X-ray diffraction. Preliminary study shows that complex **1** is active for highly cis-1,4 polymerization of isoprene (92% selectivity) in the presence of $AlEt_3$ and Me_3SiCl.

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1. Introduction

Heterogeneous silica-supported metal complexes play an important role in many important chemical processes, such as hydrocarbon oxidation [1] and olefins polymerization [2]. However, the structural details of the active centers in these silica-supported metal complexes are often difficult to be characterized due to the heterogeneous nature of the supported complexes. Preparation and characterization of soluble metallosiloxane complexes incorporating Met_x–O_y–Si_z interactions provide one of choices to investigate the structural properties of the silica-supported metal complexes [3–13].

The incompletely condensed silsesquioxanes share structural similarities with the hydroxylated silica surfaces, and a variety of metal silsesquioxanes have been synthesized and served as molecular models for metal-doped silicate surfaces [2,14–16]. On the other hand, there have been only a handful examples of the well-characterized silsesquioxane derivatives of rare-earth metals [16–20], and no example of the tetrameric rare earth metal silsesquioxanes has been reported to date. Recently, we prepared a Nd(III) silsesquioxane complex and characterized it by single crystal X-ray diffraction. The X-ray diffraction analysis revealed that the complex is a tetrameric cage complex. Herein we report these results.

2. Results and discussion

The reaction of anhydrous $NdCl_3$ with NaO^iPr in benzene/^{i}PrOH (v/v = 1:1), and subsequent treatment with trisilanol [(*i*-C_4H_9)$_7$(Si_7O_9)(OH)$_3$] in toluene gave a pale blue solid (Scheme 1). Recrystallization of the blue solid from hexane provided pale blue crystals of complex **1**. The solid-state structure of **1** was determined by X-ray crystallography. The ORTEP drawing of **1** is shown in Fig. 1, the crystallographic data are given in Table 1, and the selected bond lengths and angles are listed in Table 2.

Complex **1** is therefore a tetrameric Nd(III) silsesquioxane cage complex as shown in Fig. 1. Complex **1** consists of four silsesquioxane-Nd units, while the silsesquioxane anion chelates one Nd ion with three siloxy O atoms, two siloxy O atoms [O6 and O10] of the silsesquioxane anion further bridge two adjacent Nd ions respectively to form the tetrameric structure. Interestingly, a Cl ion (located on an intersection point of three crystallographic two-fold rotation axes) sets in the cage center and forms close contacts with four Nd ions (Nd–Cl = 2.5742 Å). Thus, each Nd ion is coordinated by five siloxy O atoms [O1, O6, O10, O6^{iii} and O10^{i}] and one Cl ion with a distorted octahedral geometry. A Na ion (located on a twofold rotation axis with 1/2 site occupancy factor) balances the charge. The structure of **1** is quite different from those of the

* Corresponding authors. Tel./fax: +86 571 87953727 (Z. Shen).
E-mail addresses: opl_sunwl@zju.edu.cn (W. Sun), zhiquan_shen@163.com (Z. Shen).

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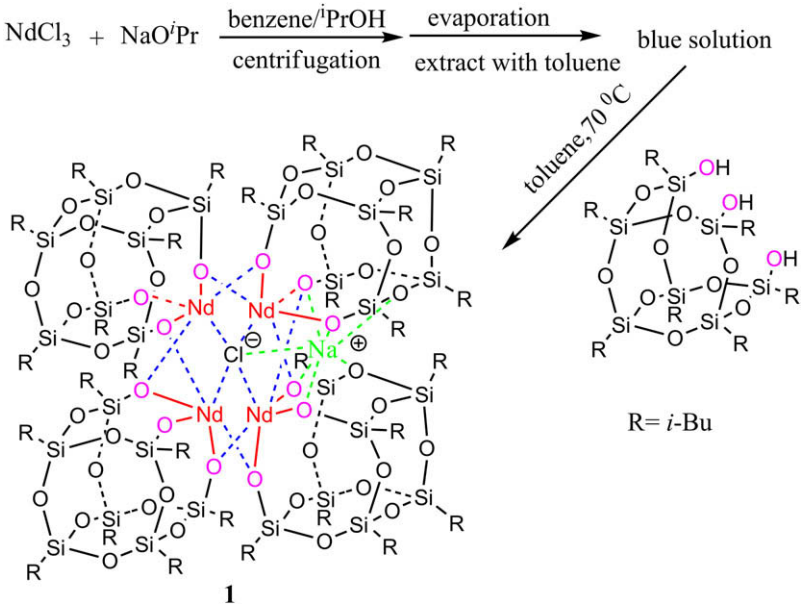

Scheme 1. Synthesis of complex **1**.

reported rare-earth metal silsesquioxane complexes, such as $[Y(III)\{(c\text{-}C_5H_9)_7Si_7O_{12}\}_2(Ph_3P{=}O)_2]$ [17], $[Ce(IV)\{(c\text{-}C_6H_{11})_8Si_8O_{13}\}_2(py)_3]$ [18], $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}\{(C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}Yb(III)Li_2(THF)_2\text{-}(MeCN)] \cdot 2.5THF$ [19], $[Sm(III)(OC_6H_3Bu^t_2\text{-}2,6)\{(c\text{-}C_5H_9)_7Si_7O_9(OLi)(O)(OTBDMS)\}_2]$ [20] and $[\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2Li_4\}\text{-}Yb(III)N(SiMe_3)_2]$ [21]. Complex **1** shares some common structural features with the reported Nd siloxane complex $\{Na_6\{[PhSiO_2]_8Nd_4(\mu_4\text{-}O)[O_2SiPh]_8\} \cdot 10EtOH \cdot 8H_2O\}$ (**2**) [22], they are both the tetrameric Nd complexes with O bridges. However, the differences between above two complexes are also significant. For example, **1** has one Cl ion in the cage center while **2** has the central oxygen; each Nd ion of **1** is coordinated by five siloxy O atoms, one of which coordinates one Nd ion and the other four O atoms interact with two Nd ions each; while in 2, each Nd ion is coordinated by six siloxy O atoms, two of which coordinates one Nd ion and the other four O atoms interact with two Nd ions each.

Cis-1,4 polyisoprene is the most important rubber. The cis-1,4 selective polymerization of isoprene provides one method to synthesize this rubber. Many catalytic systems are available for this reaction, and the rare-earth catalytic system is among the most promising [23]. The complex **1** was tested as a pre-catalyst for the isoprene polymerization using $AlEt_3$, $Al(i\text{-}Bu)_3$ or MAO as the cocatalyst. No polymer was formed, that's probably due to the lack of chloride source. Therefore, Me_3SiCl was added to the **1**/$AlEt_3$

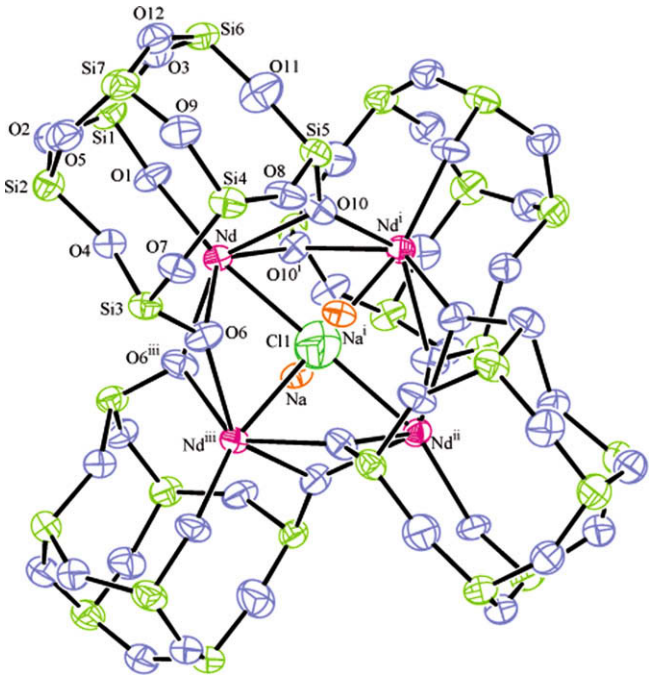

Fig. 1. ORTEP drawing of **1** with 25% probability displacement ellipsoids. C and H atoms are omitted for clarity. The site occupancy factor of the Na atom is 1/2. Symmetry codes: (i) $-x+1, y, -z+1/2$, (ii) $-x+1, -y+1/2, z$, (iii) $x, -y+1/2, -z+1/2$.

Table 1
Crystallographic data of **1**.

Empirical formula	$C_{112}H_{252}ClNaNd_4O_{48}Si_{28}$
Formula weight	3789.06
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Ccca*
a (Å)	29.694(2)
b (Å)	35.433(2)
c (Å)	20.5497(13)
Volume (Å^3)	21621(2)
Z	4
D_{calc} (mg/m^3)	1.164
Absorption coefficient (mm^{-1})	1.171
F(000)	7872
Crystal size (mm^3)	0.22 × 0.20 × 0.16
θ Range for data collection (°)	1.34–25.00
Completeness to θ = 28.28 (%)	100
Reflections collected	9535
Independent reflections [$R_{(int)}$]	3656 [0.1374]
Absorption correction	
Maximum and minimum transmission	0.830; 0.735
Data/restraints/parameters	9535/23/289
Final *R* indices($I > 2\sigma(I)$)	R_1 = 0.1064, wR_2 = 0.3118
R indices(all data)	R_1 = 0.2189, wR_2 = 0.3651
Goodness-of-fit on F^2	0.963
Largest difference peak and hole (e Å^{-3})	1.251 and −1.327

Table 2
Selected bond lengths (Å) and angles (°) in **1**.

Nd–O1	2.171(8)	O6i–Nd–O4	95.3(3)
Nd–O6	2.508(9)	O10ii–Nd–O4	167.8(3)
Nd–O6ii	2.345(9)	O10–Nd–O4	105.6(3)
Nd–O10	2.405(9)	O6–Nd–O4	55.5(3)
Nd–O10i	2.358(9)	Cl1–Nd–O4	124.07(18)
Nd–Cl1	2.5742(7)	Nd–Cl1–Ndii	89.25(3)
O6i–Nd–O6	72.8(4)	Ndii–Cl1–Ndi	178.61(4)
O10ii–Nd–O6	136.7(3)	Nd–Cl1–Ndiii	178.61(4)
O10–Nd–O6	90.1(4)	Ndii–Cl1–Ndiii	90.77(3)
O1–Nd–Cl1	160.3(3)	Ndi–Cl1–Ndiii	89.25(3)
O6i–Nd–Cl1	71.3(3)	Ndi–O6–Nd	98.0(4)
O10ii–Nd–Cl1	67.9(2)	Ndi–O6–Nai	88.7(4)
O10-Nd–Cl1	67.3(2)	Nd–O6–Nai	86.7(4)
O6–Nd–Cl1	68.9(2)	Ndii-O10–Nd	98.8(4)
O1–Nd–O4	75.6(3)		

catalytic system. With 0.027 mmol **1**, 0.677 mmol $AlEt_3$, 0.054 mmol Me_3SiCl and 40 mmol isoprene in 2 mL of toluene, the polymerization proceeded and gave a cis-1,4 polyisoprene with 60% yield in 18.5 h. The polymer has high cis-1,4 content (92%) and 8% 3,4-content. The molecular weight of the polymer is 3.35×10^3, and the polydispersity is 1.99.

3. Conclusions

In conclusion, a new tetrameric neodymium-silsesquioxane cage complex $\{[(i\text{-}C_4H_9)_7(Si_7O_{12})Nd]_4NaCl\}$ (**1**) was synthesized and characterized. The four Nd-POSS units of **1** are linked by multiple Nd–O–Nd and Nd–Cl–Nd bonding. The Nd–O–Si bonding interactions in complex **1** can be used to mimic those in the silica-supported rare-earth metal catalysts.

4. Experimental

4.1. General

All operations were carried out under an atmosphere of argon using Schlenk techniques. Anhydrous $NdCl_3$ was prepared from Nd_2O_3 and HCl according to the standard procedure [24]. NaO^iPr in benzene/^{i}PrOH was synthesized according to the literature procedure [25]. $(i\text{-}C_4H_9)_7(Si_7O_9)(OH)_3$ was purchased from Aldrich and used without further purification. Toluene and hexane were distilled from Na-benzophenone ketyl. The elemental analysis was performed on a Flash EA1112, and the content of rare-earth metal was measured by EDTA-titration method. ^{1}H NMR spectra were recorded on a Bruker Avance DMX 400 MHz spectrometer in d_6-benzene at room temperature, and the chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvent. IR spectra were recorded on a Bruker Fourier transforminfrared (FT-IR) spectrometer.

4.2. Synthesis of POSS-Nd complex (*1*)

NaO^iPr (97 mg, 1.18 mmol) in 4 mL of hot benzene/^{i}PrOH(v/v = 1:1) was added into a refluxing ^{i}PrOH solution of $NdCl_3$ (95 mg, 0.38 mmol, in 4 mL of ^{i}PrOH), the reaction mixture was refluxed overnight. The precipitate was removed by centrifugation. The clear blue solution was evaporated in vacuo to give pale blue residue. The above residue was extracted by 7 mL of toluene. $[(i\text{-}C_4H_9)_7(Si_7O_9)(OH)_3]$ (292 mg, 0.37 mmol) was added to the toluene extract, and the reaction mixture was stirred at 70 °C for 12 h. The solvent was removed in vacuo, and the pale blue residue was extracted by 7 mL of hexane. The hexane extract was concentrated to about 2 mL in vacuo, and cooled to −30 °C to give pale blue crystals of **1** (101 mg, 30% yield).

Elemental Anal. Calc. for $C_{112}H_{252}ClNaNd_4O_{48}Si_{28}$: C, 35.50; H, 6.70; Nd, 15.23. Found: C, 35.64; H, 6.68; Nd, 15.18%.

IR data (nujol, ν, cm^{-1}): 2954 s, 2928 m, 2905 m, 2871 m, 1465 m, 1401 w, 1383 w, 1366 w, 1228 w, 1080 s, 992 m, 925 m, 835 m, 739 m, 580 w, 506 w, 430 w.

^{1}H NMR (C_6D_6, δ, ppm): 2.10 (m, $^3J_{HH}$ = 6.8 Hz, $-CH_2\mathbf{CH}(CH_3)_2$); 1.10 (d, $^3J_{HH}$ = 6.4 Hz, $-CH_2CH\mathbf{(CH_3)_2}$); 0.86 (d, $^3J_{HH}$ = 6.8 Hz, $-\mathbf{CH_2}CH(CH_3)_2$). Other signals are unable to be assigned due to the paramagnetic property of the Nd complex.

4.3. Polymerization procedure

Trimethylsilane chloride (6.9 μL, 0.054 mmol) and **1** (102 mg, 0.027 mmol) in 2 ml toluene were added to a 20 mL ampule. After stirring for 0.5 h, $AlEt_3$ (0.09 mL, 0.677 mmol) was added. The catalyst solution was aged for 1 h at 60 °C, and then isoprene (4 mL, 40 mmol) was added. After 18.5 h, the polymerization was quenched with 5% HCl ethanol solution containing 1% 2,6-di-*tert*-butyl-4-methyl phenol. The resulting polymer was isolated, washed with ethanol, and dried under vacuum.

4.4. X-ray crystallography for *1*

Suitable single crystals of **1** were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structure was solved by direct methods. As isobutyl groups are disordered in the crystal structure, their geometry parameters were constrained in the refinement process. The crystal structure was refined isotropically for isobutyl-C atoms and anisotropically for the other non-H atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. A PLATON calculation indicates that the crystal structure contains solvent accessible voids of 1160 Å^3 between disordered isobutyl groups of the adjacent molecules, but no solvent molecules could be located in the difference Fourier map, resulting the larger *R* factor and smaller D_{calc} value.

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