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Silsesquioxane chemistry. Part 10. Silsesquioxane silanolate complexes of samarium and scandium[☆]

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Dedicated to Professor Oskar Glemser on the occasion of his 90th birthday

Abstract

Two novel complexes of samarium and scandium containing silsesquioxane silanolate ligands have been synthesized and structurally characterized by X-ray diffraction. Yellow $(C_5Me_5)_2Sm[\mu\text{-}Cy_7Si_8O_{12}O]_2Li(THF)$ (**1**, Cy = c-C_6H_{11}), the first organolanthanide silsesquioxane complex, has been obtained by treatment of the 'ate'-complex $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ with $Cy_7Si_8O_{12}OLi$ in a molar ratio of 1:2. In heterobimetallic **1** samarium and lithium are bridged by two silsesquioxane silanolate ligands. Reaction of $(C_5Me_5)Sc(acac)_2$ with two equivalents of $Cy_7Si_8O_{12}OH$ leads to the closely related binuclear scandium complex $[Sc(acac)_2(\mu\text{-}Cy_7Si_8O_{12}O)]_2$ (**2**). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silsesquioxanes; Samarium; Scandium; X-ray structure

1. Introduction

Polyhedral silsesquioxanes are in the focus of current interest in organosilicon chemistry. Their general formula $(RSiO_{1.5})_n$ places them formally between silica (SiO_2) and the silicones $(R_2SiO)_n$. Silsesquioxanes play an important role in catalysis research [1–5] as well as materials science [6–8]. Well-characterized silsesquioxane derivatives of the Group 3 and lanthanide elements are still rare, although the first lanthanide silsesquioxanes have already been reported in 1994 by Herrmann et al. [10]. Among the few recent examples are e.g. $Cy_7Si_7O_{12}Ln(THF)_2$ (Ln = Y, La) [11], a heterobimetallic lithium–ytterbium derivative [12] and $Sm(OC_6H_3tBu_2\text{-}2,6)[(c\text{-}C_5H_9)_7Si_7O_9(O)(OLi)(OSiMe_2tBu)]_2$ [13]. Here we wish to report the use of the cuboctameric silsesquioxane silanol $Cy_7Si_8O_{12}OH$ in the preparation of Group 3 metal and lanthanide derivatives, including the first *organo*lanthanide silsesquioxane complex. Such silsesquioxane silanols have recently been proposed as interesting model systems to mimic isolated silanol sites in partially dehydroxylated silica [14].

2. Results and discussion

The starting material $Cy_7Si_8O_{12}OH$ was prepared in close analogy to a published procedure in two steps by treatment of $Cy_7Si_7O_9(OH)_3$ with $SiCl_4$ in the presence of triethylamine, followed by hydrolysis of the intermediate chlorosilane $Cy_7Si_7O_{12}Cl$ [14]. Metalation of $Cy_7Si_8O_{12}OH$ with methyllithium in diethylether proceeded smoothly at room temperature to afford $Cy_7Si_8O_{12}OLi$, which was used in situ for further reactions.

The synthesis of an organosamarium derivative was achieved as illustrated in Eq. (1) by the reaction of $Cy_7Si_8O_{12}OLi$ with the readily available 'ate'-complex $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ [15] in a 2:1 molar ratio.

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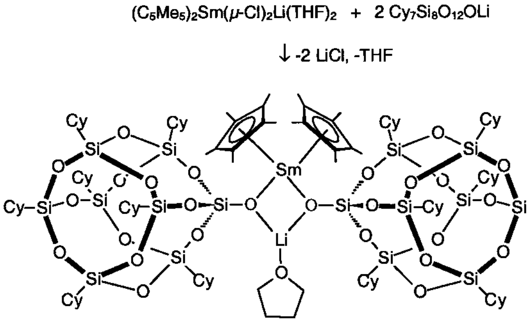


1

(1)

Compound **1** was isolated after continuous extraction of the crude product with diethylether in 68% yield in the form of bright yellow, air-sensitive crystals. ^{1}H- and ^{13}C-NMR data indicated the presence of THF in the samples. ^{29}Si-NMR spectroscopy had earlier been demonstrated to be a very useful tool for the characterization of silsesquioxane complexes [14]. The sensitivity of this method is sufficiently high to distinguish between very similar complexes, and integrated relative intensities normally agree well with the expected stoichiometries. In the case of **1** the ^{29}Si-NMR spectrum shows eight resonances of the same intensity, indicating that all silicon atoms of the $Cy_7Si_8O_{12}$ cage are chemically non-equivalent despite the C_{3v} symmetry of the ligand. This was confirmed by an X-ray diffraction study, which revealed the presence of a heterobimetallic complex in which samarium and lithium are bridged by two silsesquioxane silanolate ligands (Fig. 1). Compound **1** is the first *organo*lanthanide complex containing silsesquioxane derivatives as ligands.

Structurally, complex **1** is related to the starting material $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ [15] in that the bridging chlorine ligands have been replaced by bulky silsesquioxane silanolate groups. Presumably due to their steric bulk only one THF ligand is now sufficient to saturate the coordination sphere around lithium, which is in contrast to the 'ate'-complex $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ in which Li is four-coordinated. For a comparison of structural details, the literature holds only a small number other samarium complexes containing Si–O-based ligands, namely $Sm(OC_6H_3t\text{Bu}_2\text{-}2,6)[(c\text{-}C_5H_9)_7Si_7O_9(O)(OLi)(OSiMe_2t\text{Bu})]_2$ [13], $(\mu\text{-}OSiMe_2OSiMe_2O)[(C_5Me_5)_2Sm(THF)]_2$ [17], and the tetraphenyldisiloxanediolate derivative $[\{(Ph_2SiO)_2O\}Li(DME)]_2SmCl(DME)$ (DME = 1,2-dimethoxyethane) [18]. The latter compound displays a similar bonding situation as in **1** in that the formally anionic disiloxanediolate oxygen atoms act as bridges between samarium and lithium. The Sm–O distances in $[\{(Ph_2SiO)_2O\}Li(DME)]_2SmCl(DME)$ are in the range of 231.3(3)–235.1(2) pm as compared with 231.6(4) pm in **1**. Here, too, the main difference is the tricoordination of Li in **1** in contrast to a distorted tetrahedral coordination geometry around lithium in the heterobimetallic disiloxanediolate complex.

A different synthetic approach was chosen to synthesize a related scandium silsesquioxane complex. Treatment of $(C_5Me_5)Sc(acac)_2$ [16] with the free silanol $Cy_7Si_8O_{12}OH$ in refluxing toluene (Eq. (2), molar ratio 1:1) resulted in elimination of pentamethylcyclopentadiene and formation of the novel binuclear scandium complex $[Sc(acac)_2(\mu\text{-}Cy_7Si_8O_{12}O)]_2$ (**2**).

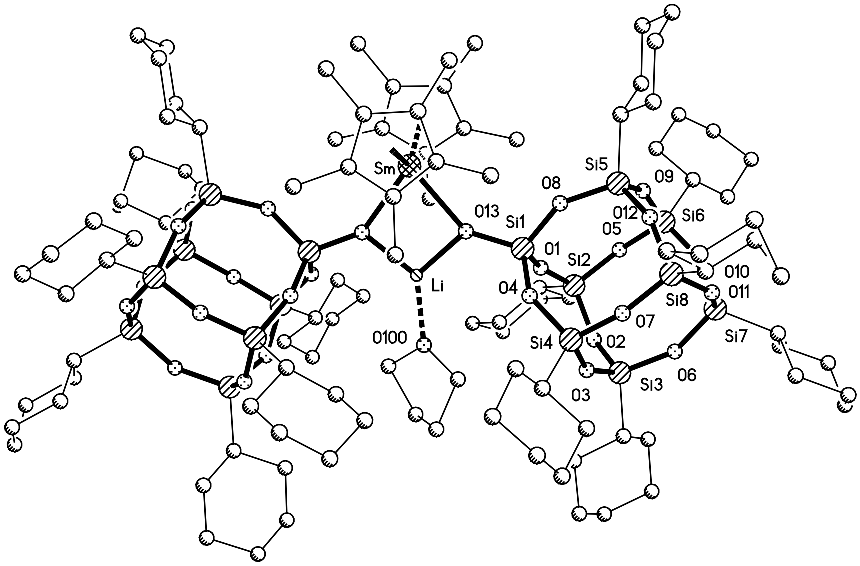


Fig. 1. Structure of **1** in the crystal. Selected interatomic distances (pm) and bond angles (°): Sm–O13 231.6(4), Sm–C93 272.4(7) (shortest Sm–C bond), Sm–C91 277.0(7) (longest Sm–C bond), O13–Li 187.7(9), Li–O100 193.0(15), Si1–O13 159.1(4), Si1–O1 161.6(5); O100–Li–Sm, O13–Li–O100, Li–O13–Sm 91.9(3), Si1–O13–Li 121.0(4), Si1–O13–Sm 147.0(2).

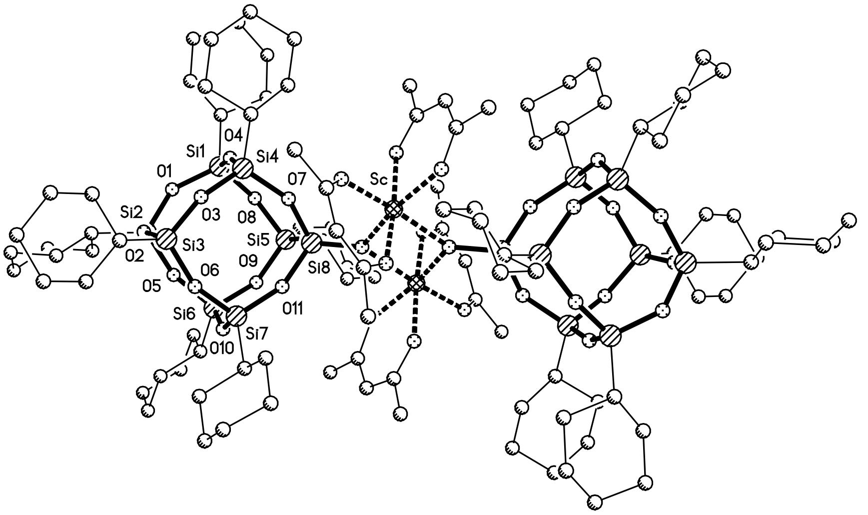
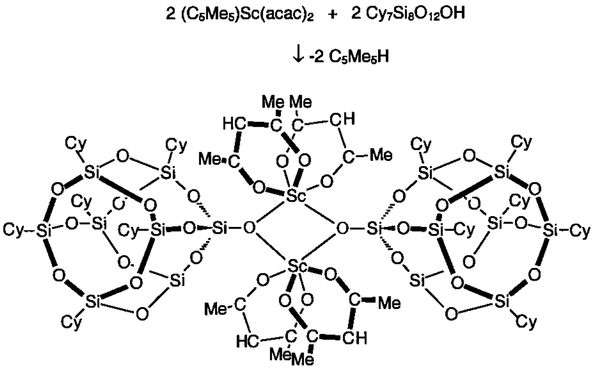


Fig. 2. Structure of **2** in the crystal. Selected interatomic distances (pm) and bond angles (°): Sc–O17 208.1(3), Sc–O13 211.3(3) Sc–O13 # 1 212.5(3), Sc–Sc # 1 329.75(14), Si1–O1 162.6(3); O13–Sc–O13 # 1 77.83(11), O16–Sc–O13 163.99(12).



2

(2)

Colorless single-crystals of **2** suitable for X-ray diffraction were obtained by fractional crystallization from pentane. Fig. 2 shows the molecular structure of **2** revealing a dimeric molecule in which two $Sc(acac)_2$ units are symmetrically bridged by the mono-anionic silsesquioxane silanolate ligands.

Compound **2** represents the first example of a scandium complex containing silsesquioxane derivatives as ligands. To the best of our knowledge, the only closely related compound is the trinuclear scandium disiloxanediolate complex $[(Ph_2Si_2O)_2O]_2Sc_3(acac)_5$ which has been prepared in a similar manner by treatment of $(C_5Me_5)Sc(acac)_2$ with 1,1,3,3-tetraphenyldisiloxanediol [18]. With an average of 213.0(2) pm, the Sc–O(μ-OSi) distances in this complex are virtually identical with those in **2**.

In summarizing these results, it has been demonstrated that the silsesquioxane silanolate ligand $Cy_7Si_8O_{12}O^-$ is well suited for the synthesis of Group 3 metal and lanthanide derivatives. Such complexes can be prepared either by metathetical reactions using $Cy_7Si_8O_{12}OLi$ and the corresponding metal halides or by protonation of suitable precursors with the free silanol. The resulting products can be regarded as models for lanthanide catalysts grafted on partially dehydroxylated silica.

3. Experimental

All reactions were carried out under an atmosphere of dry nitrogen with the use of standard Schlenk techniques or dry boxes (M. Braun). Solvents were carefully dried over Na–benzophenone and freshly distilled prior to use. IR spectra were recorded on a Perkin–Elmer FTIR spectrometer system 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (^1H 400.13 MHz, ^{13}C 101.62 MHz, ^{29}Si 79.49 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C) or an internal standard (^1H, ^{29}Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS932 apparatus. Melting and decomposition points (m.p. (dec.)) were measured on an Electrothermal IA 9100 apparatus. The compounds $Cy_7Si_7O_9(OH)_3$ [9], $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ [15], and $(C_5Me_5)Sc(acac)_2$ [16] were prepared according to literature procedures.

3.1. Preparation of $(C_5Me_5)_2Sm[\mu\text{-}Cy_7Si_8O_{12}O]_2Li(THF)$ (1)

To a solution of 2.00 g (1.96 mmol) $Cy_7Si_8O_{12}OH$ in 40 ml THF was added methyllithium (1.25 ml of a 1.6 M solution in diethylether, ≅ 1.97 mmol) and the mixture was stirred for 1 h at room temperature (r.t.) to ensure complete metalation. This was followed by addition of solid $(C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ (0.65 g, 1.0 mmol). After stirring for 24 h, the solvent was removed in vacuo. The solid residue was transferred onto a filter frit, washed with hexane and continuously extracted with diethylether (ca. 40 ml). Cooling of the ether extract to 5 °C for 3 days afforded 1.69 g (68%) **1** as yellow crystals. M.p. ca. 320 °C (dec.). IR (KBr, ν(cm^{-1})): 2923vs, 2850vs, 1525w, 1448s, 1348w, 1327w, 1294w, 1269m, 1197s, 1110vs, 1028s, 999s, 895s, 850m, 826w, 743w, 604w, 550m, 516vs, 476s, 415s. ^{1}H-NMR (C_6D_6): δ 3.98 (s br, 4 H, THF), 2.10–0.70 (complex m, 188 H, C_5Me_5, CH_2 and CH of $C_6H_{11}Si$, THF) ppm. ^{13}C-NMR (C_6D_6): δ 115.99 (***C***$_5$Me$_5$), 68.85 (THF), 28.09, 27.93, 27.75, 27.63, 27.59, 27.29, 27.23, 27.12, 27.06 (***C***H$_2$ *c*-C_6H_{11}), 26.76 (THF), 23.78, 23.61, 23.53 (***C***H *c*-C_6H_{11}) ppm. ^{29}Si-NMR (C_6D_6): δ −67.00, −67.31, −67.50, −67.61, −68.04, −68.44, −99.48, −113.25 ppm. Anal. Calc. for $C_{108}H_{192}LiO_{27}Si_{16}Sm$ (2529.37) C, 51.29; H, 7.65. Found: C, 51.07; H; 7.93%

3.2. Preparation of [Sc(acac)$_2$(μ-Cy$_7$Si$_8$O$_{12}$O)]$_2$ (2)

2.00 g (1.96 mmol) $Cy_7Si_8O_{12}OH$ and 0.75 g (1.98 mmol) (C_5Me_5)Sc(acac)$_2$ were suspended in toluene (50 ml) and the mixture was stirred at reflux temperature for 2 h. The resulting slightly turbid solution was filtered while hot and concentrated in vacuo to a total volume of 30 ml. Cooling to −5 °C for 3 days afforded a crystalline material, which was still contaminated with small amounts of Sc(acac)$_3$ (a minor by-product present in the starting material (C_5Me_5)Sc(acac)$_2$). Analytically pure, colorless crystals were obtained by fractional crystallization from pentane. Yield: 1.50 g (61%). M.p. 280–283 °C (dec.). IR (KBr, ν(cm^{-1})): 2920vs, 2850vs, 2793w, 1590vs, 1526vs, 1448vs, 1396vs, 1327w, 1276s, 1197vs, 1104vs, 1026vs, 950s, 912m, 895s, 850s, 826m, 810w, 770m, 743w, 662m, 610m, 516vs, 475s, 414vs. ^{1}H-NMR (C_6D_6): δ 5.28 (s, 4H, CH$_3$COC***H***COCH$_3$), 1.71 (s, 24H, C***H***$_3$COCHCOC***H***$_3$), 2.2–0.95 (complex m, 154H, $CH_2 + CH$ *c*-C$_6$***H***$_{11}$) ppm. ^{13}C-NMR (C_6D_6): δ 191.88 (***C***=O, acac), 103.45 (***C***H, acac), 28.25, 27.87, 27.82, 27.75, 27.52, 27.44, 27.35, 27.31, 27.16 (***C***H$_2$ *c*-C_6H_{11}), 26.66 (***C***H$_3$, acac), 24.07, 23.89, 23.83, 23.56 (***C***H c-C_6H_{11}) ppm. ^{29}Si-NMR (C_6D_6): δ −66.97, −67.62, −68.01, −68.24, −105.25 ppm. Anal. Calc. for $C_{104}H_{182}O_{34}Sc_2Si_{16}$ (2515.84) C, 49.65; H, 7.27. Found: C, 50.06; H, 7.81%.

Table 1
Summary of crystal structure determination data for **1** and **2**

	1	**2**
Formula	$C_{108}H_{184}LiO_{27}$-$Si_{16}Sm$	$C_{104}H_{182}O_{34}Sc_2$-Si_{16}
M_r	2529.37	2515.84
Habit, color	Column, yellow	Plate, colorless
Crystal dimension (mm)	0.41 × 0.18 × 0.14	0.55 × 0.35 × 0.15
Crystal system	Orthorhombic	Monoclinic
Space group	*Fddd*	*C*2/*c*
Unit cell constants		
a (Å)	25.290(2)	34.311(2)
b (Å)	43.308(2)	18.871(1)
c (Å)	52.342(2)	27.358(2)
β (°)	90	120.978(3)
V (Å^3)	57 330	15 872
Z	16	4
$D_{x(\mathrm{calc})}$ (mg m^{-3})	1.176	1.100
μ (mm^{-1})	0.604	0.276
F(000)	21 520	5376
T (°C)	−100(2)	−75(2)
$2\theta_{\max}$ (°)	52.2	56.6
Reflections collected	77 175	48 912
Independent reflections	14 173	18 558
R_{int}	0.106	0.043
Refined parameters	715	707
wR (F^2, all reflections)	0.222	0.269
R ($F > 4\sigma(F)$)	0.087	0.086
S	1.08	1.09
Maximum Δ/σ	−0.157	0.001
Maximum $\Delta\rho$ (e Å^{-3})	1.81	2.25

3.3. X-ray structure determinations (cf. Table 1)

All measurements were performed on a Siemens SMART CCD system with Mo–K$_\alpha$ X-ray radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Selected crystals of **1** and **2** were coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. As an absorption correction THE SADABS routine was applied. The crystal structures were solved by direct methods (SHELXTL [19]) and refined using the program SHELXL 97 [20].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 178212 (**1**) and CCDC 178213 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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