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# Tris(trimethylsilyl)siloxides of gadolinium and lanthanum: synthesis, structure and some properties

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## Abstract

A series of gadolinium and lanthanum siloxide complexes of empirical formula  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{Ln}(\text{L}_n)$  {Ln = Gd,  $\text{L}_n = (\text{THF})_2$  (**1**),  $(\text{MeCN})_2$  (**2**),  $[\text{N}(\text{C}_2\text{H}_4)_3\text{N}]_2$  (**3**),  $(4,4'\text{-dipyridyl})_2$  (**4**),  $(4,4'\text{-dipyridyl})_1$  (**5**); Ln = La,  $\text{L}_n = (\text{THF})_4$  (**6**)} have been prepared by the reaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  (Ln = Gd, La) with  $(\text{Me}_3\text{Si})_3\text{SiOH}$  or  $\text{LnCl}_3$  (Ln = Gd) with  $(\text{Me}_3\text{Si})_3\text{SiONa}$  in various solvents. Both  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{Gd}(\text{THF})_2$  (**1**) and  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{Gd}[\text{N}(\text{C}_2\text{H}_4)_3\text{N}]_2$  (**3**) have been characterized by X-ray crystallography. The Gd in both **1** and **3** has a trigonal-bipyramidal environment with three O atoms in equatorial and two B atoms (B = O in **1** and N in **3**) in axial positions. The symmetries of molecules of **1** and **3** are  $C_{3i}$  and  $C_{3h}$ , respectively. The Gd–O–Si angles and the Gd–O distances are  $161.2(3)^\circ$ ,  $2.142(7)$  Å in **1** and  $165.4(2)^\circ$ ,  $2.161(4)$  Å in **3**. The Gd–O(THF) distances in **1** are  $2.448(9)$ ,  $2.314(18)$  and the Gd–N distance in **3** is  $2.520(6)$  Å. Gadolinium complex (**1**) and the lanthanum complex (**6**) readily absorb one and three moles of  $\text{CO}_2$ , respectively to form the corresponding carbonates. Compounds **1** and **6** sublime at  $205^\circ\text{C}$  in vacuo to form homoleptic siloxides. A subsequent rise in temperature results in their decomposition to give polylanthanosiloxanes, and  $(\text{Me}_3\text{Si})_3\text{SiOH}$  as the only volatile product up to  $300^\circ\text{C}$ . © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Lanthanides; Silicon; Siloxides; X-ray diffraction

## 1. Introduction

It is known that metal alkoxides  $\text{M}(\text{OR})_n$  are versatile potential candidates that meet the requirements for sol–gel conversion to metal-oxide materials. Many p- and d-metal alkoxides are used for these purposes [1–4] in contrast to lanthanide alkoxides [5]. The reason for this is that the majority of lanthanide alkoxides possess more complicated structures and their hydrolysis in the presence of other hydrolysed substrates gives heterogeneous gels. However, the presence of lanthanides as additives in polycomponent gels is potentially important in the production of new materials and catalysts [1,6,7].

The simple alkoxides  $(\text{RO})_3\text{Ln}$ , (R = Me, Et) are

polymeric compounds with poor solubility and they do not meet the requirements of sol–gel processing [2]. The degree of association of alkoxides with more bulky substituents may be varied widely and depends on the nature both of R and Ln as well as the methods of preparation and isolation. Moreover, the products of apparently simple reactions  $\{3\text{RONa} + \text{LnCl}_3\}$  are very often cluster compounds, containing halogen, alkaline metal, interstitial oxygen or other elements, and the yield of the products is hard to reproduce [8]. On the other hand, some of the compounds with bulky ligands, for instance  $\text{R}_2\text{C}_6\text{H}_3\text{O}$  (R = alkyl) and  $\text{Ph}_3\text{SiO}$ , are monomeric [9–12], but these ligands are hard to remove from the gel after hydrolysis. Preparation of bi- or polycomponent gels or combined organic–inorganic materials [13] using a lanthanide component is a more difficult problem because of the considerable differences between the rates of hydrolysis of the various compo-

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nents. In this regard, the generation of compounds with novel ligands remains an important problem. In this light tris(trimethylsilyl)siloxy derivatives possess some advantages. The tris(trimethylsilyl)siloxy group is sufficiently bulky and provides good solubility of compounds in hydrocarbons, and a relatively low rate of hydrolysis. Moreover, tris(trimethylsilyl)silanol is also highly soluble in all organic solvents, it may easily be evaporated in vacuo (81°C/1.5 Torr) and its synthesis is quite simple [14,15]. Here we wish to report the synthesis, structure and some properties of tris(trimethylsilyl)siloxides of gadolinium and lanthanum and their adducts with Lewis bases.

## 2. Experimental

### 2.1. General considerations

The solvents were purified prior to use following standard methods [16]. The compounds La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> [17], Gd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> [17], (Me<sub>3</sub>Si)<sub>3</sub>SiOH [14,15], (Me<sub>3</sub>Si)<sub>3</sub>SiONa [14] were prepared according to known methods. The reagents 1,4-diazabicyclo[2.2.2]-octane, 4,4'-dipyridyl were obtained commercially (Aldrich) and purified by vacuum sublimation prior to use. All manipulations were performed in vacuum or under an argon atmosphere using standard Schlenk techniques.

Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer from 4000 to 200 cm<sup>-1</sup>. Room-temperature magnetic moments were measured by the Faraday method. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> solutions using Tesla BS-487-C (80 MHz) device, with CHCl<sub>3</sub> as internal standard.

Thermal decomposition of compounds **1** and **6** was carried out in vacuo (or in an argon atmosphere) with a heating rate of 3° min<sup>-1</sup>. The temperature range studied extended from 20 to 300°C.

Gas chromatography analyses of products of hydrolysis were carried out on a Tsvet-500 chromatograph, equipped with stainless steel columns 0.4 cm × 200 cm, packed with 5% SE-30 on Chromatone N-Super, with a thermoconductivity detector and with helium as carrier gas.

### 2.2. Synthesis of [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>3</sub>Gd(THF)<sub>2</sub> (**1**)

(A) A mixture of Gd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (0.95 g, 1.5 mmol) and tris(trimethylsilyl)silanol (1.20 g, 4.5 mmol) in 25 ml of THF was stirred for 2 h at 50°C. The solvent and hexamethyldisilazane were removed in vacuo to give colourless crystals which were recrystallised from THF. Yield 1.58 g (92%). Anal. Calc. for C<sub>35</sub>H<sub>97</sub>Si<sub>12</sub>O<sub>5</sub>Gd: C, 38.49; H, 8.95; Gd, 14.39. Found: C, 38.21; H, 9.04; Gd, 14.45. IR (Nujol, cm<sup>-1</sup>): 1235 (vs), 840 (vs) (SiMe); 900 (s) (SiOGd); 1020 (m) (C–O, THF); 740 (w), 675 (s), 620 (s) (SiC), 400 (m).

(B) A suspension of 0.45 g of GdCl<sub>3</sub> (1.7 mmol) in 15 ml of THF was added to a solution of 1.45 g (5.1 mmol) of sodium tris(trimethylsilyl)siloxide in 20 ml of THF. The mixture was stirred for 3 h at 60°C. Tetrahydrofuran was evaporated in vacuo at 20°C and replaced with 30 ml of hexane. Subsequent stirring for 1 h and filtration to remove the NaCl precipitate yielded a clear solution. Concentration in vacuo and crystallisation from warm hexane afforded large crystals which are identical to the crystals obtained by method A as shown by X-ray diffraction.

### 2.3. Synthesis of [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>3</sub>Gd(MeCN)<sub>2</sub> (**2**)

Tris(trimethylsilyl)silanol (1.20 g, 4.5 mmol) in 10 ml of MeCN was added to a solution of Gd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (0.95 g, 1.5 mmol) in 15 ml of MeCN at 20°C. An abundant fine crystalline solid immediately precipitated. The solvent was decanted. The residue was washed with pure MeCN and dried in vacuo. Recrystallisation from toluene gave large crystals of **2**. Yield: 1.30 g (85%). Anal. Calc. for C<sub>31</sub>H<sub>87</sub>Si<sub>12</sub>O<sub>3</sub>N<sub>2</sub>Gd: C, 36.14; H, 8.51; N, 2.72; Gd, 15.26. Found: C, 35.87; H, 8.59; N, 2.83; Gd, 15.33. M.w. 1030; Found: 1017 (cryoscopy in benzene). IR (Nujol, cm<sup>-1</sup>): 1240 (s), 840 (vs) (SiMe); 1260 (w), 1290 (w), 1020 (s), 930 (w, sh.) (MeCN); 910 (m) (SiOGd).

### 2.4. Interaction of **1** with 1,4-diazabicyclo[2.2.2]-octane (DABCO). Synthesis of [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>3</sub>Gd[N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N]<sub>2</sub> (**3**)

DABCO (0.17 g, 1.5 mmol) in 10 ml of toluene was added to a solution of **1** (0.83 g, 0.76 mmol) in 20 ml of toluene. The resulting solution was maintained for 12 h at 20°C then concentrated in vacuo to 5 ml. Large colourless crystals suitable for X-ray diffraction precipitated overnight at 0°C. The supernatant was decanted, and the remaining crystals were washed with cold toluene and dried in vacuo. Yield 0.67 g (75%). Anal. Calc. for C<sub>39</sub>H<sub>105</sub>N<sub>4</sub>O<sub>3</sub>Si<sub>12</sub>Gd: C, 39.95; H, 9.03; Gd, 13.41. Found: C, 40.45; H, 9.13; Gd, 14.21. IR (Nujol, cm<sup>-1</sup>): 1235 (vs), 840 (vs) (SiMe); 900 (s) (SiOGd); 1310 (w), 1050 (m), 990 (w) (C–N); 670 (s), 615 (m) (SiC<sub>3</sub>); 400 (m).

### 2.5. Interaction of **1** with 4,4'-dipyridyl

#### 2.5.1. Synthesis of [(Me<sub>3</sub>Si)<sub>3</sub>SiO]<sub>3</sub>Gd(4,4'-dipy)<sub>2</sub> (**4**)

An excess of 4,4'-dipyridyl (1.29 g, 8.27 mmol) in 15 ml of THF was added to a solution of **1** (3.05 g, 2.76 mmol) in 20 ml of THF. The mixture was maintained for 2 h at 50°C. Following concentration in vacuo to 10 ml and crystallization overnight at 0°C yields pale-yellow crystals. The supernatant was decanted and the remaining crystals were washed with cold THF and

dried in vacuo. Yield 2.82 g (81%). Anal. Calc. for  $C_{47}H_{97}N_4O_3Si_{12}Gd$ : C, 44.78; H, 7.76; Gd, 12.47. Found: C, 44.05; H, 7.83; Gd, 12.21. IR (Nujol,  $cm^{-1}$ ): 1240 (s), 840 (vs) (SiMe); 900 (m) (SiOGd); 670 (m), 615 (m) (SiC<sub>3</sub>); 1575 (s), 1400 (m), 800 (w) (4,4'-dipyridyl).

### 2.5.2. Synthesis of a coordination polymer $\{[(Me_3Si)_3SiO]_3Gd(4,4'-dipy)\}_n$ (**5**)

Acetonitrile (40 ml) was added to a solution of **4** (3.15 g, 2.50 mmol) in 10 ml of THF. The mixture was stirred for 2 h at 20°C. An amorphous yellow solid precipitated. The precipitate was removed by filtration and washed with acetonitrile and dried in vacuo. Yield 2.53 g (92%). Anal. Calc. for  $C_{37}H_{89}N_2O_3Si_{12}Gd$ : C, 40.24; H, 8.12; N, 2.54; Gd, 14.24. Found: C, 41.01; H, 8.25; N, 2.41; Gd, 14.35. IR (Nujol,  $cm^{-1}$ ): 1235 (s), 840 (vs) (SiMe); 900 (s) (SiOGd); 670 (m), 615 (m) (SiC<sub>3</sub>); 1595 (m), 1400 (vw), 800 (vw) (4,4'-dipyridyl). The remaining filtrate was evaporated in vacuo. The residue (white water-soluble crystals) contained almost pure 4,4'-dipyridyl. Hydrolysis of **5** in THF affords a white precipitate of  $Gd(OH)_3$ . The filtrate contained  $(Me_3Si)_3SiOH$  and 4,4'-dipyridyl in the molar ratio 3.1:1 according to quantitative GLC-data. Note that tris(trimethylsilyl)silanol and 4,4'-dipyridyl form a stable crystalline complex in the molar ratio 1:1 according to <sup>1</sup>H-NMR data (ppm): 8.02–8.79 (d, 4H), 7.60–7.58 (d, 4H), 0.24 (27H).

### 2.6. Synthesis of $\{[(Me_3Si)_3SiO]_3La(THF)_3\} \cdot THF$ (**6**)

Tris(trimethylsilyl)silanol (1.61 g, 6.1 mmol) in 10 ml of THF was added to a solution of  $La[N(SiMe_3)_2]_3$  (1.07 g, 2.0 mmol) in 15 ml of THF. The mixture was stirred for 3 h at 50°C. The solvent and hexamethyldisilazane were removed in vacuo to give colourless crystals which were recrystallised from THF. Yield: 2.02 g (83%). Anal. Calc. for  $C_{43}H_{113}Si_{12}O_7La$ : C, 42.39; H, 9.35; La, 11.40. Found: C, 42.15; H, 9.29; La, 11.29. IR (Nujol,  $cm^{-1}$ ): 1240 (s), 840 (vs) (SiMe); 900 (m) (SiOLa); 1040 (s) (THF). <sup>1</sup>H-NMR (ppm): 0.00 (s, 81H); 3.88 (s, 16H); 1.90 (s, 16H).

### 2.7. Interaction of $[(Me_3Si)_3SiO]_3Gd(THF)_2$ (**1**) with carbon dioxide

An ampoule was charged with a solution of **1** (0.90 g, 0.82 mmol) in THF and attached to a burette containing CO<sub>2</sub>. The solution was stirred slowly. After 10 min the volume of absorbed CO<sub>2</sub> was 18 ml (0.82 mmol). Then the absorption stopped. The solvent was removed in vacuo to afford fine needle crystals, which were recrystallised from THF to form  $[(Me_3Si)_3SiO]_2GdO_2COSi(SiMe_3)_3(THF)_2$ . Yield 0.85 g (91%). Anal. Calc. for  $C_{36}H_{97}Si_{12}O_7Gd$ : C, 38.05; H, 8.60; Gd, 13.84.

Found: C, 37.97; H, 8.56; Gd, 13.88. IR (Nujol,  $cm^{-1}$ ): 1235 (vs), 840 (vs) (SiMe); 930 (s) (SiOGd); 1020 (m) (C–O, THF); 740 (w), 675 (s), 620 (s) (SiC), 1550 (s) (RCO<sub>2</sub>).

### 2.8. Interaction of $\{[(Me_3Si)_3SiO]_3La(THF)_3\} \cdot THF$ (**6**) with carbon dioxide

An ampoule was charged with a solution of **6** (0.85 g, 0.70 mmol) in THF and attached to a burette containing CO<sub>2</sub>. The solution was stirred slowly. After 10 min the volume of absorbed CO<sub>2</sub> was 47 ml (2.1 mmol). Then the absorption stopped. The solvent was removed in vacuo to afford fine needle crystals, which were recrystallised from THF to form  $\{[(Me_3Si)_3SiOCO_2]_3La(THF)_2\}$ . Yield 0.88 g (93%). Anal. Calc. for  $C_{38}H_{97}Si_{12}O_{11}La$ : C, 37.84; H, 8.11; La, 11.52. Found: C, 37.71; H, 8.18; La, 11.46. IR (CCl<sub>4</sub>,  $cm^{-1}$ ): 1235 (vs), 840 (vs) (SiMe); 1020 (m) (C–O, THF); 740 (w), 675 (s), 620 (s) (SiC), 2320 (w) (CO<sub>2</sub>), 1675 (s), 1530 (vs), 1380 (s), 1290 (s), 1250 (sh) (RCOO).

### 2.9. Thermal decomposition

Solid state thermolysis of compounds **1** and **6** was carried out under steady vacuum pumping by slow heating of the samples (3° min<sup>-1</sup>) from 20 to 300°C. Homoleptic compounds,  $[(Me_3Si)_3SiO]_3Ln$  (Ln = La, Gd) sublimes at 205°C (0.01 mm Hg) to give crystalline products. Anal. Calc. for  $C_{27}H_{81}Si_{12}O_3Gd$ : C, 34.20; H, 8.61; Gd, 16.58. Found: C, 34.55; H, 8.47; Gd, 16.35. IR (Nujol,  $cm^{-1}$ ): 1235 (vs), 840 (vs) (SiMe); 900 (s) (SiOGd); 740 (w), 675 (s), 620 (s) (SiC), 400 (m). Anal. Calc. for  $C_{27}H_{81}Si_{12}O_3La$ : C, 34.88; H, 8.78; La, 14.94. Found: C, 34.95; H, 8.87; La, 14.75. <sup>1</sup>H-NMR (ppm): 0.02(s, 81H). IR (Nujol,  $cm^{-1}$ ): 1240 (s), 840 (vs) (SiMe); 900 (m) (SiOLa).

Further raising of the temperature results in decomposition of the complexes. The only volatile product,  $(Me_3Si)_3SiOH$ , separated out of the samples (ca. 1.5 equivalents) above 220°C, and was detected by GLC-analysis. IR ( $cm^{-1}$ ): 3620, 3420 (O–H), 1240, 840 (SiMe), 1040 (Si–O). <sup>1</sup>H-NMR (ppm): 0.16 (27H, Me), 1.25 (1H, OH). The solid yellow–brown residue contains, according to IR-data, Si–O–Si modes (1050  $cm^{-1}$ , br), SiMe (broad absorptions at 840 and 1240  $cm^{-1}$ ) and Gd–O–Si modes (910  $cm^{-1}$  weak, br.).

### 2.10. X-ray diffraction studies

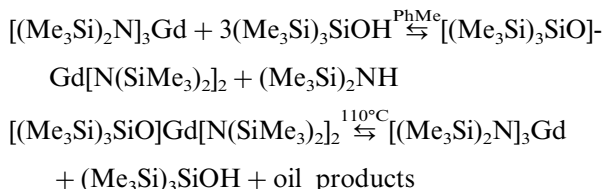
The colourless crystals of **1** and **3** were grown by slow cooling to room temperature of hot solutions of the compounds in hexane or toluene, respectively. The crystals were removed from a Schlenk tube under a stream of Ar and covered with a layer of hydrocarbon

oil. A suitable crystal was selected, attached with grease to a glass fibre and placed in the low-temperature device of an X-ray diffractometer. All X-ray data were collected on a Siemens P3/PC diffractometer at 158 (**1**) and 153 (**3**) K. The THF molecules in **1** are disordered into three positions (see Fig. 1) and refined with fixed multiplicity of 0.333 for the C(10), C(11), C(12), C(13) atoms and their symmetrical equivalents. The H atoms of THF molecules were not taken into account. All calculations were performed using the SHELXTL-PLUS package [18]. The crystal data and some details of the data collection and refinement for **1** and **3** are given in Table 1. Selected bond distances and angles in **1** and **3** are given in Tables 2 and 3, respectively.

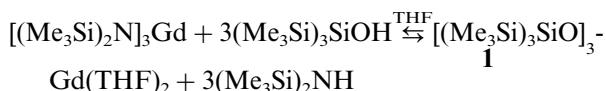
### 3. Results and discussion

Taking into account the sterically demanding nature of the tris(trimethylsilyl)siloxy group, we hoped to synthesise the homoleptic gadolinium tris(trimethylsilyl)siloxide,  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{Gd}$ , without coordinated solvent molecules. However, the reaction of three equivalents of  $(\text{Me}_3\text{Si})_3\text{SiOH}$  with  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Gd}$  in toluene was found to proceed incompletely and affords a waxy solid. Only one equivalent of  $(\text{Me}_3\text{Si})_2\text{NH}$  was released. Subsequent heating up to 110°C in vacuo affords the starting material  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Gd}$ ,  $(\text{Me}_3\text{Si})_3-$

SiOH and oily products. When the reaction proceeds in a non-coordinating solvent, the chemical equilibrium seems to take place due to the low acidity of tris(trimethylsilyl)silanol:



It should be noted that more acidic triphenylsilanol,  $\text{Ph}_3\text{SiOH}$ , reacts with some of the lanthanide silylamides in toluene to afford homoleptic insoluble polymeric compounds  $[\text{Ln}(\text{OSiPh}_3)_3]_n$  ( $\text{Ln} = \text{La}, \text{Y}$ ) [10]. The low solubility of the latter compounds also favoured the shift in the chemical equilibrium to the right. In our case both the products and the starting compounds are soluble. So, the use of a coordinated solvent is necessary. When the reaction was carried out in THF, compound **1** was obtained in good yield:



The same compound was prepared by interaction of gadolinium chloride with sodium tris(trimethylsilyl)siloxide. Gadolinium chloride is dissolved over several minutes, after addition of the sodium silanolate:

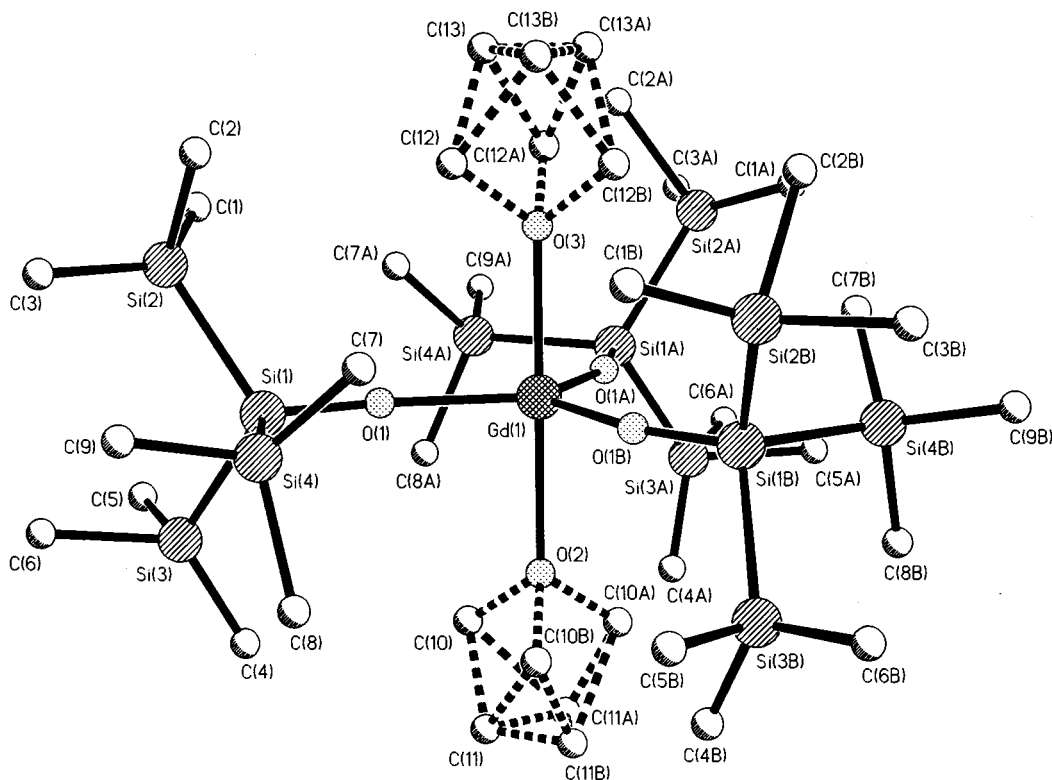
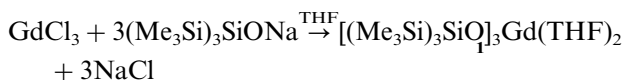


Fig. 1. X-ray structure of **1**. The disordered positions of THF molecules are shown by solid dashed lines.

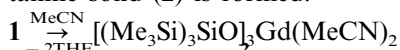
Table 1  
Summary of crystallographic data and some details of data collection and refinement for **1** and **3**

Compound	<b>1</b>	<b>3</b>
Diffractometer	Siemens P3/PC	Siemens P3/PC
Formula	$[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{-Gd}(\text{THF})_2$	$[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{-Gd}[\text{N}(\text{C}_2\text{H}_4)_3\text{N}]_2$
MW	1028.3	2345.2
<i>T</i> (K)	158	153
Radiation	Mo-K $\alpha$	Mo-K $\alpha$
Crystal size (mm)	0.30 × 0.30 × 0.40	0.4 × 0.50 × 0.60
Crystal system	Hexagonal	Hexagonal
Space group	<i>P</i> 6 <sub>3</sub>	<i>P</i> 6 <sub>3</sub> / <i>m</i>
Unit cell		
<i>a</i> (Å)	14.716(5)	14.890(5)
<i>c</i> (Å)	16.843(10)	17.215(4)
<i>V</i> (Å <sup>3</sup> )	3159(2)	3307(2)
<i>Z</i>	2	2
Absorption correction	N/A	N/A
2 $\theta$ range (°)	2.0–50.0	2.0–50.0
No. of collected reflections	1712	4568
No. of observed reflections	1310	1414
	( <i>F</i> > 6.0 $\sigma$ ( <i>F</i> ))	( <i>F</i> > 4.0 $\sigma$ ( <i>F</i> ))
Hydrogen atoms	Riding model, fixed isotropic <i>U</i>	Riding model, fixed isotropic <i>U</i>
Data to parameter ratio	6.6:1	14.7:1
GOF ( <i>F</i> <sup>2</sup> )	1.08	1.31
Final <i>R</i> indices (observed reflections) (%)	<i>R</i> = 4.49, <i>R</i> <sub>w</sub> = 5.71	<i>R</i> = 3.92, <i>R</i> <sub>w</sub> = 5.68
<i>R</i> indices (all data) (%)	<i>R</i> = 5.35, <i>R</i> <sub>w</sub> = 8.95	<i>R</i> = 4.34, <i>R</i> <sub>w</sub> = 6.86
Diff. peak, hole (e Å <sup>-3</sup> )	0.54, –0.71	0.72, –0.67



The ate-complex,  $[(\text{Me}_3\text{Si})_3\text{SiO}]_2\text{Gd}[(\text{Me}_3\text{Si})_3\text{SiO-}\mu_2]_2\text{Na}(\text{THF})_2$ , is not formed as the product of this reaction even when a four-fold excess of sodium tris(trimethylsilyl)siloxide was used. Large crystals of **1** were grown from warm hexane solution by slow cooling. The crystals prepared in both cases were shown by X-ray powder diffraction to be identical, and the structure was confirmed by X-ray crystallography.

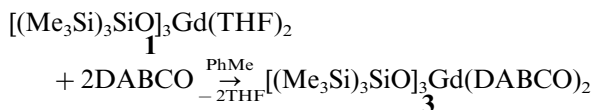
Compound **1** is soluble in hydrocarbons and THF but sparingly so in acetonitrile. After a work-up of a toluene solution of **1** with MeCN, a new white crystalline solid (**2**) is formed:



A crystalline precipitate of **2** is also readily formed when  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Gd}$  reacts with  $(\text{Me}_3\text{Si})_3\text{SiOH}$  in acetonitrile. However, the reaction of  $\text{GdCl}_3$  with  $(\text{Me}_3\text{Si})_3\text{SiONa}$  in acetonitrile is not successful because the C≡N triple bond is cleaved by sodium silanolate. The acetonitrile adduct **2** is stable toward intramolecular cleavage of the C≡N bond presumable because of the less ionic character of the Gd–O bond.

The reactions of gadolinium siloxide (**1**) with bidentate nitrogen ligands were undertaken in order to study the possibility of formation of one-dimensional coordination polymers. Such ligands as 1,4-diazabicyclo[2.2.2]octane (DABCO) and 4,4'-dipyridyl are known to form extended one-dimensional structures with a series of transition metal complexes [19].

We have studied the interaction of gadolinium siloxide (**1**) with DABCO in toluene at different molar ratio of the reagents (1:1, 1:2, 1:3, 2:1, respectively). In all cases the only product **3** of composition 1:2 was formed.



Attempts to prepare a coordination polymer (where molar ratio Gd: DABCO = 1:1) also led instead to the

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

Bond length (Å)	
Gd(1)–O(1)	2.142(7)
Gd(1)–O(2)	2.448(9)
Gd(1)–O(3)	2.314(18)
Si(1)–O(1)	1.644(7)
Si(1)–Si(2)	2.389(10)
Si(1)–Si(3)	2.322(11)
Si(1)–Si(4)	2.341(3)
Si(2)–C(1)	1.751(13)
Si(2)–C(2)	1.983(14)
Si(2)–C(3)	1.869(14)
Si(3)–C(4)	1.727(18)
Si(3)–C(5)	1.900(15)
Si(3)–C(6)	1.867(18)
Si(4)–C(7)	1.864(19)
Si(4)–C(8)	1.939(20)
Si(4)–C(9)	1.856(13)
O(2)–C(10)	1.483(17)
O(3)–C(12)	1.513(20)
Bond angle (°)	
O(1)–Gd(1)–O(2)	89.2(4)
O(1)–Gd(1)–O(3)	90.8(4)
O(2)–Gd(1)–O(3)	180.0
O(1)–Gd(1)–O(1)	120.0
Gd(1)–O(1)–Si(1)	161.2(3)
O(1)–Si(1)–Si(2)	113.3(6)
O(1)–Si(1)–Si(3)	113.0(6)
O(1)–Si(1)–Si(4)	109.0(2)
Si(2)–Si(1)–Si(3)	105.2(3)
Si(2)–Si(1)–Si(4)	109.6(4)
Si(3)–Si(1)–Si(4)	106.5(4)
Si(1)–Si(2)–C(1)	115.4(7)
Si(1)–Si(2)–C(2)	109.0(6)
Si(1)–Si(2)–C(3)	107.7(5)
Si(1)–Si(3)–C(4)	117.7(8)
Si(1)–Si(3)–C(5)	112.3(6)
Si(1)–Si(3)–C(6)	113.9(6)
Si(1)–Si(4)–C(7)	108.6(5)
Si(1)–Si(4)–C(8)	110.3(6)
Si(1)–Si(4)–C(9)	112.9(5)

Table 3  
Selected bond distances (Å) and angles (°) in **3**

<i>Bond length (Å)</i>	
Gd(1)–O(1)	2.161(4)
Gd(1)–N(1)	2.520(6)
Si(1)–Si(3)	2.375(2)
Si(1)–Si(2)	2.357(3)
Si(1)–O(1)	1.641(5)
Si(2)–C(1)	1.856(12)
Si(2)–C(2)	1.847(9)
Si(3)–C(3)	1.819(9)
Si(3)–C(4)	1.848(11)
Si(3)–C(5)	1.872(7)
N(1)–C(6)	1.473(5)
N(2)–C(7)	1.444(6)
C(6)–C(7)	1.522(7)
<i>Bond angle (°)</i>	
O(1)–Gd(1)–N(1)	90.0
O(1)–Gd(1)–O(1A)	120.0
N(1)–Gd(1)–N(1A)	180.0
Si(3)–Si(1)–Si(2)	107.3(1)
Si(3)–Si(1)–O(1)	113.5(1)
Si(2)–Si(1)–O(1)	110.2(1)
Si(3)–Si(1)–Si(3A)	104.5(1)
Si(1)–Si(3)–C(3)	112.1(3)
Si(1)–Si(3)–C(4)	111.9(3)
Si(1)–Si(3)–C(5)	112.7(2)
Si(1)–Si(2)–C(1)	111.6(3)
Si(1)–Si(2)–C(2)	112.0(3)
Si(1)–Si(2)–C(2A)	112.0(3)
Gd(1)–O(1)–Si(1)	165.4(2)
Gd(1)–N(1)–C(6)	111.5(3)
C(6)–N(1)–C(6A)	107.4(3)
C(7)–N(2)–C(7A)	108.6(4)
N(1)–C(6)–C(7)	110.8(4)

complex **3**. Apparently, the existence of a coordinate polymer is prevented by steric factors, the DABCO ligand being too small in comparison with the large size of the organosilicon branched moiety. As a consequence, the methyl groups of adjacent fragments  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{Gd}$  will hinder stable coordination of two gadolinium centres to one DABCO molecule. It should be noted that the gadolinium silylamide,  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Gd}$ , does not react with DABCO or 4,4-dipyridyl due to steric constraints.

### 3.1. X-ray structure of **1** and **3**

The X-ray structure of compounds **1** and **3** are shown in the Figs. 1 and 2, respectively. In both cases the Gd atom has a trigonal-bipyramidal environment with three O atoms in equatorial and two B atoms (B = O in **1** and N in **3**) in axial positions. The symmetries of the molecules of **1** and **3** are  $C_{3i}$  and  $C_{3h}$ , respectively.

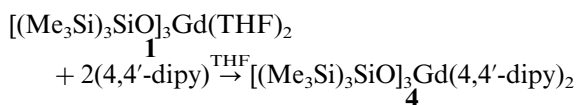
The Gd–O–Si angles in **1** and **3** (161.2(3) and 165.4(2)°, respectively) can be compared with the corresponding angles in other lanthanide and yttrium com-

pounds containing bulky groups: 158.9° in  $\text{Gd}(O-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$  [20], 157.8–174.6° in  $\text{Y}(\text{OSiPh}_3)_3[\text{OP}(n\text{-Bu})_3]_2$  [21], 168.5–174.4° in six-coordinate  $[\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3]\cdot\text{THF}$  [21], 163.7° for the Yb–Se–Si angle in  $\text{Yb}[\text{SeSi}(\text{SiMe}_3)_2](\text{TMEDA})_2$  [22] and 130.64, 164.45° for Yb–Te–Si angles in  $\{\text{Eu}[\text{TeSi}(\text{SiMe}_3)_2](\text{DMPE})_2\}_2(\mu\text{-DMPE})\}$  [22]. In both structures the angles at the Si(1) atoms are somewhat distorted (105.2(3)–113.3(6)° in **1** and 104.5(1)–113.5(1)° in **3**) and at the Si(2), Si(3) and Si(4) atoms—the angles are slightly increased (107.7(5)–115.4(7)° in **1** and 116.6(3)–112.7(2)° in **3**) from the ideal tetrahedral angle of 109.47° (Tables 2 and 3).

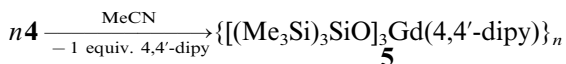
The Gd–O(Si(Si(Me)<sub>3</sub>)<sub>3</sub>) distances in **1** and **3** (2.142(7) and 2.161(4) Å, respectively) are close to the average Gd–O distance (2.130 Å) in the gadolinium complex  $\text{Gd}(O-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$  with a similar coordination mode [20] and the Y–O distances in the above-mentioned yttrium compounds  $[\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3]\cdot\text{THF}$  2.12–2.14 Å [21],  $\text{Y}(\text{OSiPh}_3)_3[\text{OP}(n\text{-Bu})_3]_2$  2.121–2.129 Å [21] and in the anion  $\text{Y}(\text{OSiPh}_3)_4(\text{DME})^-$  2.143–2.196 Å [21].

The THF molecules in **1** are disordered (Fig. 1). The Gd–O(THF) distances in **1** are different (2.314(18) and 2.448(9) Å) and can be comparable to analogous lengths of this bond in  $\text{Gd}(O-2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)_3(\text{THF})_2$  2.39 Å [20]. The Gd(1)–N(1) distance in **3** is 2.520(6) Å.

The length of bidentate 4,4'-dipyridyl is almost two times longer than DABCO, so it can easily coordinate gadolinium atom at each nitrogen. Indeed, we have synthesised two types of complexes {1:(coordination polymer) and 1:2}. Interaction of gadolinium siloxide (**1**) with excess of 4,4'-dipyridyl in THF follow by solvent removal yields pale-yellow crystals of **4**:



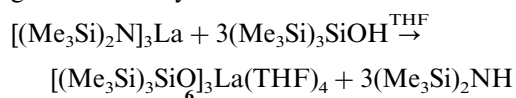
The coordination polymer can be prepared in two ways: using an equivalent mixture of **1** and 4,4'-dipyridyl and by treatment of **4** with excess acetonitrile. In the latter case, the yellow fine crystalline precipitate of **5** was formed and one equivalent of 4,4'-dipyridyl remains in the mother liquor:



There are some differences in the IR spectra of the complexes **4** and **5**. The spectrum of compound **4** shows the presence of SiMe modes (1240 (s), 835 (vs), 670 (m)); Si–O–Gd modes (900 m) and the bands corresponding to 4,4'-dipyridyl ligands: 1575 (s), 1400 (m), 800(w). The IR spectrum of coordinate polymer **5** shows the same absorption for MeSi and GdOSi modes but different ones assigned to the 4,4'-dipy- ligand. Thus, the band at 1575 cm<sup>-1</sup> is shifted by 15 cm<sup>-1</sup> to 1590 cm<sup>-1</sup>; the absorptions at 1400 and 800 cm<sup>-1</sup> are

reduced in intensity. It should be noted that the analogous changes in IR spectra were observed for coordinate polymers of transition metals bearing bridged 4,4'-dipyridyl ligands [19] in contrast to monomer complexes,  $R_nM(4,4'\text{-dipy})_2$ , where dipyridyl bands are not shifted and remain of the same intensity as those ones inherent to the free base.

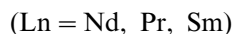
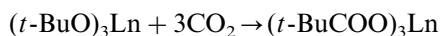
Lanthanum silylamide,  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{La}$ , reacts with tris(trimethylsilyl)silanol in a manner similar to the gadolinium silylamide:



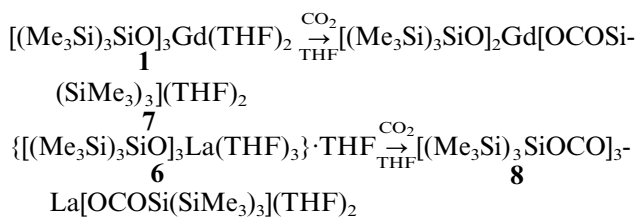
At ambient temperature, the  $^1\text{H-NMR}$  spectrum of the compound **6** revealed a singlet assigned to the  $(\text{Me}_3\text{Si})_3\text{SiO-}$  group and resonances for only one type of THF ligand. Integration of the  $^1\text{H}$  spectrum established the  $(\text{Me}_3\text{Si})_3\text{SiO-}$  to THF ratio to be 3: 4. We assign these data to the structure  $[(\text{Me}_3\text{Si})_3\text{SiO}]_3\text{La}(\text{THF})_3 \cdot \text{THF}$  that is the analogue of the triphenylsiloxy derivative prepared by Caulton and co-workers [10].

### 3.2. Interaction with carbon dioxide

It is known that lanthanide (III) alkoxides readily absorb three moles of  $\text{CO}_2$  to form insertion products [23]:



Surprisingly, gadolinium siloxide **1** absorbs only one mole of carbon dioxide in contrast to the corresponding lanthanum derivative:



This is, perhaps, due to both the smaller ionic radius of gadolinium and its basicity. Infrared spectra of compounds **7** and **8** have new bands at 1250, 1360 and 1580  $\text{cm}^{-1}$  that correspond to the carbonate group. Moreover, compound **8** shows absorption at 2320  $\text{cm}^{-1}$ , typical of coordinated carbon dioxide. Interestingly, the GdOSi band in **7** (930  $\text{cm}^{-1}$ ) is shifted by 30  $\text{cm}^{-1}$  relative to the starting siloxide **1**.

### 3.3. Thermal stability

The new gadolinium and lanthanum tris(trimethylsilyl)siloxides show quite high thermal stability. Slow heating of the complexes **1** and **6** up to 190°C results in THF loss along with formation of homoleptic complexes that sublime at 200–205°C (0.01 mm Hg).

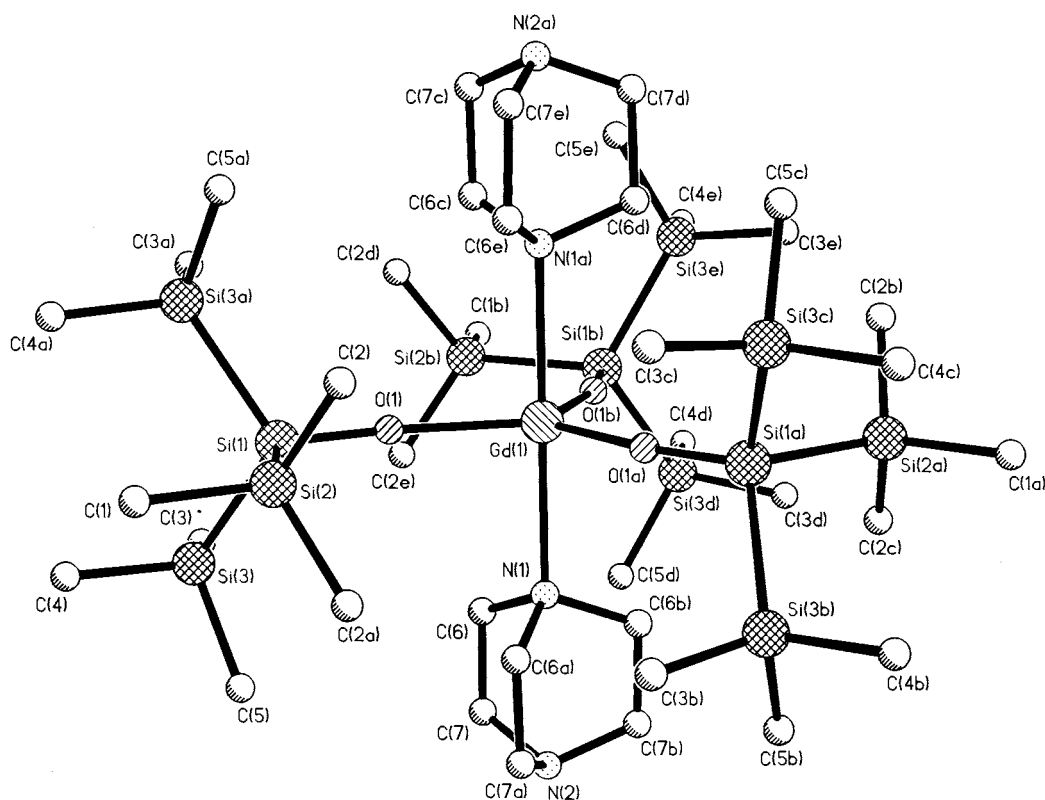
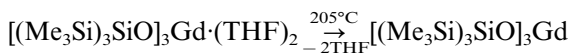


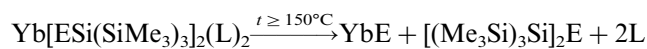
Fig. 2. X-ray structure of **3**.



A subsequent rise in the temperature caused the decomposition of the complexes. The only volatile product (up to 300°C) is tris(trimethylsilyl)silanol. The solid residue comprises insoluble polylanthanosiloxane according to IR spectroscopic data. The thermal stability of the organometallosiloxanes, it should be noted, depends on the degree of covalence of the M–O(Si) bond and the comparative affinity of silicon and metal atoms towards oxygen. Thus, the decomposition of sodium and lithium tris(trimethylsilyl)siloxides begins at 110°C to form a complex mixture of the products:  $\text{H}_2$ ,  $(\text{Me}_3\text{Si})_3\text{SiH}$  (the main product, 55%),  $\text{Me}_3\text{SiOSi}(\text{SiMe}_3)_3$  (10%), and  $(\text{Me}_3\text{Si})_3\text{SiOH}$  (13%) [14]. The thermal decomposition of ferrous ate-complex,  $\{(\text{Me}_3\text{Si})_3\text{SiO}-\text{Fe}[\mu-\text{OSi}(\text{SiMe}_3)_3]_2\text{Na}(\text{DME})\}$  begins even at 160°C [24], to form two main products: disiloxane,  $(\text{Me}_3\text{Si})_3\text{SiOSiMe}_3$ , and tetrakis(trimethylsilyl)silane,  $(\text{Me}_3\text{Si})_4\text{Si}$ . So in this case two processes take place: rearrangement with insertion of an oxygen atom into the Si–Si bond, and migration of one  $\text{Me}_3\text{Si}$  group to the  $(\text{Me}_3\text{Si})_3\text{Si}$  fragment. In contrast, the decomposition of lanthanide silanolate is not accompanied by catalytic rearrangements, only the very stable silanol,  $(\text{Me}_3\text{Si})_3\text{SiOH}$ , is formed perhaps by hydrogen radical abstraction from the nearby methyl group of a neighbouring substituent. Thus, it is logical to propose that the solid residue formed after thermolysis contains complex clusters with Gd–C and Gd–O bonds.

It is relevant to compare the thermal properties of compounds **1** and **6** with those of other known bulky lanthanide siloxides. So, homoleptic neodymium tris(tri-*t*-butyl)siloxide,  $(t\text{-Bu}_3\text{SiO})_3\text{Nd}$ , sublimes at 250°C (10<sup>−3</sup> mm Hg) [5] and decomposes at temperatures above 340°C. Thus, the tris(trimethylsilyl)siloxy-group appears to be more labile than a tris(tri-*t*-butyl)siloxy-fragment.

It is interesting to note that lanthanide derivatives of the sulphur and tellurium analogues of tris(trimethylsilyl)silanol both decompose at lower temperatures, and give different products from thermal decomposition [25]:



E = Se, Te; L = tetramethyl-ethylenediamine

The great affinity of lanthanides and silicon towards oxygen favours the high stability of lanthanide-containing organosilicon complexes and polymers. Moreover, there is some information that lanthanide silanolate additives result in the extraordinary stabilisation of silicones [26].

Thus, a series of gadolinium and lanthanum tris(trimethylsilyl)siloxide complexes with various donor coordinated molecules have been prepared and characterised. Further studies concerning to the prepa-

ration of bi- and polycomponent gels using a lanthanide components are in progress, and detailed results will be introduced in the nearest future.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 117648 for compound **1** and No. 117647 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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