

Formation and X-ray structure of [[O(Ph₂SiONa)₂]₄ · (NaOH) · (H₂O) · (7 pyridine)] · (toluene) · (pyridine) incorporating a unique assembly of three fused Na₄O₄ cubane units and a μ₃-water molecule

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Received 2 January 1997

Abstract

We report on the isolation and molecular structure of [[O(Ph₂SiONa)₂]₄ · (NaOH) · (H₂O) · (7pyridine)] · (pyridine) · (toluene) from toluene/pyridine solutions of [O(Ph₂SiONa)₂ · Py] in air; a unique structural assembly, of three edge-shared Na₄O₄ siloxane-bridged cubes, sharing one μ₆-OH site, where one cube corner is occupied by a μ₃-OH₂ group. © 1998 Elsevier Science S.A.

Keywords: Sodium; Metallasiloxane; Bridging water; Crystal structure

1. Introduction

The co-ordination chemistry of α,ω-siloxane diolates [(R₂SiO)_nO]²⁻ represents one area of metallasiloxane chemistry [1] which also covers metal complexation by a range of other important siloxanolate ligand types, for example, species with RSiO₃, R₂SiO₂, and R₃SiO functionalities. Some of these compounds are of interest as precatalysts for olefin polymerisation or as precursors for metaloxide/silica materials [1]. In recent years we have described synthesis structure and catalytic activity of a number of co-ordination compounds derived from the dilithium and disodium derivatives of the disiloxane diol [(Ph₂SiOH)₂O]₂ [2]. In this paper we report on the characterisation of the disodium derivative and a product of its hydrolysis in air.

2. Results and discussion

The disodium tetraphenyldisiloxanediolate compound formulated as [O(Ph₂SiONa)₂ · Py] (1), was formed as described in Section 4 below. The colourless moisture sensitive crystalline compound may be isolated on cooling hot toluene/pyridine 3:1 solutions. While solvent

dependency precluded structural characterisation of (1) by X-ray diffraction, similarities between the ATRIR pattern of (1) and that of the crystallographically characterised dimeric dilithium analogue (see (a) and (b) in Fig. 1) suggest a similar core structure might obtain for both. Compound (1) has been used to transfer the ligand [(Ph₂SiO)₂O]²⁻ to a range of main group and transition metals [2]. In the course of initial attempts to crystallise (1) accidental exposure of a solution of (1) to air gave colourless crystals of a new compound (2) (IR pattern (c) in Fig. 1) with composition [[O(Ph₂SiONa)₂]₄ · NaOH · H₂O · 8pyridine · (toluene) as determined by X-ray crystallography. In subsequent preparations toluene/pyridine solutions of (1) were left in a sealed flask under air at -25°C. The colourless crystalline compound obtained was subsequently stored and manipulated under a nitrogen atmosphere and had an identical infrared spectrum to that of (2). On standing in air solid samples of compound (2) underwent further change as evidenced by splitting and broadening of the infrared bands at 1000 and 1400 cm⁻¹. There was however no evidence for uptake of water or formation of -Si-OH.

3. Structure of (2)

The structure (excluding pyridine solvate) is composed of four equivalents of [O(Ph₂SiONa)₂], one

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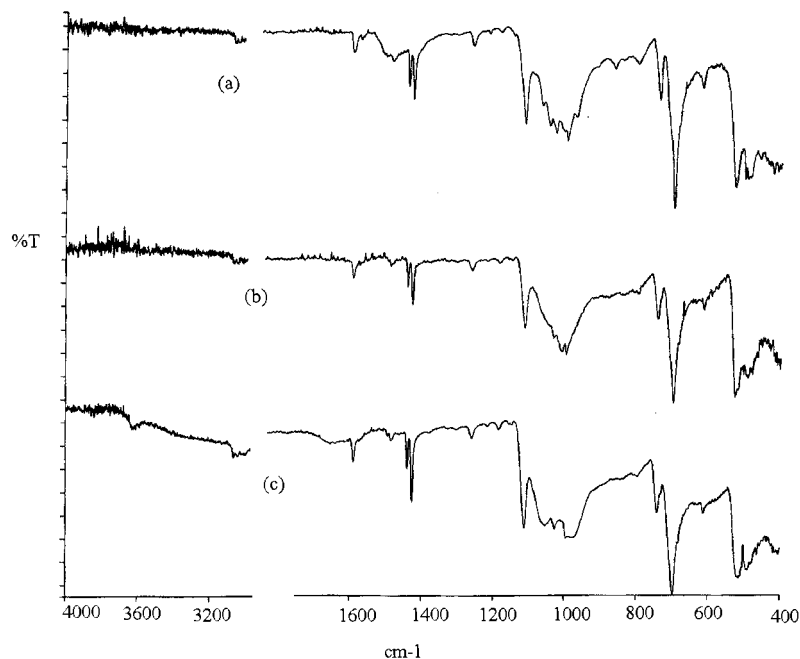


Fig. 1. ATR IR spectra of (a) $[\text{O}(\text{Ph}_2\text{SiONa} \cdot \text{Py})_2]_2$, (b) $[\text{O}(\text{Ph}_2\text{SiOLi} \cdot \text{Py})_2]_2$, and (c) $[\{\text{O}(\text{Ph}_2\text{SiONa})_2\}_4] \cdot \text{NaOH} \cdot \text{H}_2\text{O} \cdot 8\text{pyridine} \cdot (\text{toluene})$.

equivalent of NaOH, and one water molecule. The structure of (2) is shown in Fig. 2 along with selected bond lengths and angles. The basic building block

within the structure is that of the cubane Na_4O_4 unit. There are three such edge-shared units stacked in the form of a pyramid around a shared $\mu_6\text{-OH}$ group. The

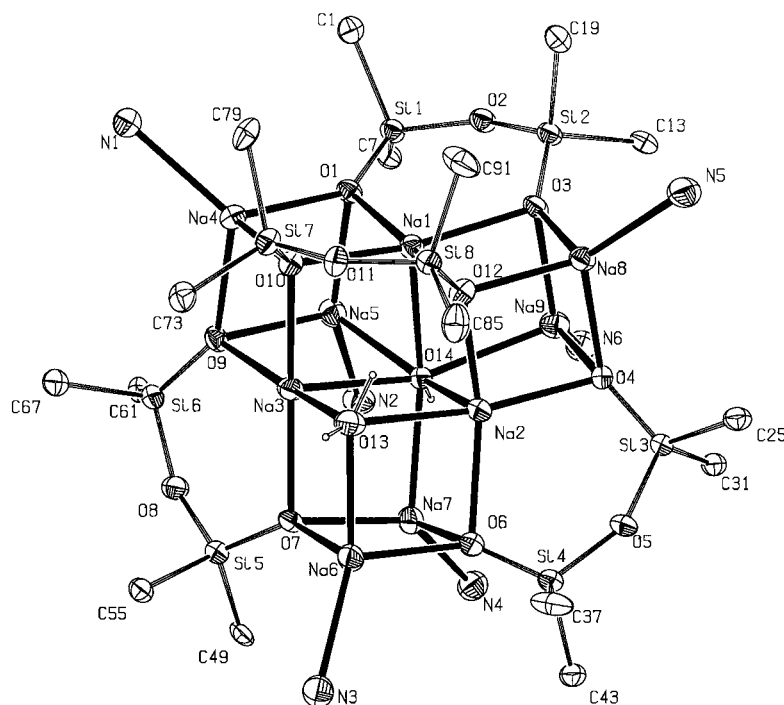


Fig. 2. Molecular structure of (2). Selected bond length (\AA) and angle ($^\circ$) averages and ranges. td = tetrahedral, sp = square pyramidal, av = average: $\text{Na}_{\text{td}}\text{-O}(\text{Si})$ 2.239–2.297(2), $\text{Na}_{\text{sp}}\text{-O}(\text{Si})$ 2.303–2.454(2), $\text{Na-O}(14)_{\text{av}}$ 2.513(2), $\text{Na}_{\text{td}}\text{-O}(13)_{\text{av}}$ 2.489(2), $\text{Na}(2)\text{-O}(13)$ 2.574(2), $\text{Na}(3)\text{-O}(13)$ 2.468(3), $\text{Na}_{\text{td}}\text{-N}_{\text{av}}$ 2.471, $\text{O}(14)\text{-H}(1\text{H})$ 0.79(3), $\text{O}(13)\text{-H}(1\text{W})$ 0.93(3), $\text{O}(13)\text{-H}(2\text{W})$ 0.75(4), $\text{Si-O}(\text{Na})_{\text{av}}$ 1.585(2), $\text{Si-O}(\text{Si})_{\text{av}}$ 1.643(2), $(\text{Si})\text{O-Na-O}(\text{Si})_{\text{av}}$ 86.42(7)–99.47(7), Si-O-Si 135.52(14)–151.7(2), $\text{Na-O}(\text{Si})\text{-Na}$ 81.53(6)–98.77(7), $\text{O}(\text{Si})\text{-Na-O}(13)$ 75.61(7)–89.67(8), $(\text{Si})\text{O-Na-O}(14)$ 90.34(7)–101.48(8), $\text{O}(14)\text{-Na}(2)\text{-O}(13)_{\text{av}}$ 92.49(8), $\text{O}(14)\text{-Na}(3)\text{-O}(13)_{\text{av}}$ 91.81(8), $\text{Na-O}(13)\text{-Na}_{\text{av}}$ 89.18(8), $\text{Na-O}(14)\text{-Na}$ 76.06(6)–88.24(7), $\text{H}(1\text{W})\text{-O}(13)\text{-H}(2\text{W})$ 118(3).

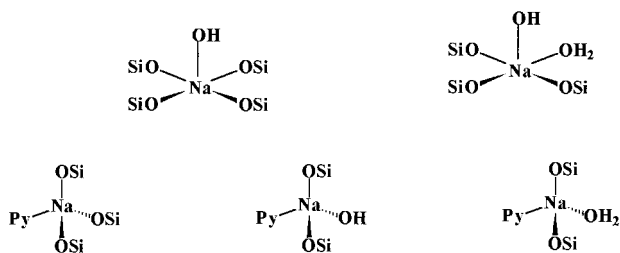


Fig. 3. Coordination environments of sodium in (2).

Na_4O_4 cubane unit is found in many other metalloorganic sodium compounds for example, tetrakis(μ_3 -hexafluoroisopropoxo)-sodium [3,4], tetrakis(μ_3 -4-methylphenoxo)-dimethoxyethane-sodium [5]. The fused assembly of three such Na_4O_4 units as seen in compound (2) is we believe unique in the metalloorganic chemistry of sodium. Similar structural motifs have been identified in polyoxoiron [6] and polyoxovanadium [7] complexes. Each Na_4O_4 unit shares two edges with neighbouring units. Alternate corners in each of the Na_4O_4 units are variously occupied by sodium in the 4- or 5-coordination environments, or one of μ_3 -O(Si), μ_6 -OH or μ_3 -OH₂. Thus there are five distinct coordination environments for sodium in the structure (see Fig. 3). The overall structure is built around the central μ_6 -OH group. There are no apparent hydrogen bonds associated with this 6-coordinate hydroxyl group proton. One striking and unusual feature of the structure (2) concerns the μ_3 -H₂O group where the water oxygen is strongly interacting with three sodiums at Na–O distances 2.468(2), 2.574(2) and 2.425(2) Å. For comparison the Na–O(Si) distances in (2) are in the range 2.239–2.454 Å and are similar to those found in $[\text{Na}\{\text{OSi}(\text{OH})\text{Bu}^t\}_2] \cdot \text{THF}$ [8] and $[\text{Cr}\{\text{O}(\text{SiPh}_2\text{O})_2\}_2] \cdot \mu\text{-Na}(\text{THF})_2$ [9]. A number of examples of compounds having water in the bridging co-ordination mode (μ_2 -OH₂) have been reported [10–16]. We are not aware of other examples of triply bridging water (μ_3 -OH₂). Recent theoretical studies [17] on the water molecule point to an orbital picture of the non-bonding electrons that is significantly different from the classical valence bond picture of doubly occupied lone pairs and such models might be important in connection with μ_3 -OH₂. The bond distances and angles within the siloxane unit are normal, there are structural similarities in the way these groups $\text{Ph}_2\text{SiOSiPh}_2$ bridge the edges of adjacent Li_2O_2 units in the step frame-work of the dilithium compounds $[\text{O}(\text{Ph}_2\text{SiOLi} \cdot \text{Py})_2]_2$ [18] and the bridging found between the corner sites of the edge-shared cubane units of (2).

It is not possible from the ²⁹Si and ²³Na NMR spectra to determine whether compound (2) retains its structural integrity in solution. The solution phase ²⁹Si NMR and the ²³Na NMR spectra of (2) each showed one signal, the latter having a linewidth of ~ 1600 Hz.

4. Experimental

Standard Schlenk methods were employed for the synthesis of (1). NMR spectra were recorded on Bruker AW-300 (²⁹Si, 59.6 MHz), Bruker AMX-600 (²³Na, 158.7 MHz). Micro-analytical data were obtained from University College London.

4.1. Preparation of $[\text{O}(\text{Ph}_2\text{SiONa})_2 \cdot \text{Py}]$

A solution of $[\text{O}(\text{Ph}_2\text{SiOH})_2]$ (5.0 g, 12 mmol) in THF (25 cm³), was added dropwise to a fine dispersion of sodium metal (0.55 g, 24 mmol) in toluene (50 cm³) at 0°C. The mixture was warmed to room temperature and then held at the reflux temperature for several hours until all of the sodium had reacted. The solution was concentrated (to 15 cm³) and filtered. Pyridine (5 cm³) was added and the mixture was subsequently heated until transparent. On slow cooling colourless (solvent dependent) crystals of (1) (6.24 g, 45.6%) formed. M.p. 212°C. Found: C, 64.95; H, 5.17; N, 2.56. Calc. for $\text{C}_{29}\text{H}_{25}\text{O}_3\text{NSi}_2\text{Na}_2$: C, 64.8; H, 4.7; N 2.6. ¹H NMR (250 MHz, C₆D₆): δ 8.20(m), 7.75(m), 7.10(m), 6.60(m).

Table 1
Crystal data and structure refinement

Identification code	ss60
Empirical formula	$\text{C}_{143}\text{H}_{131}\text{N}_8\text{Na}_9\text{O}_{14}\text{Si}_8$
Formula weight	2617.19
Temperature	150 K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	$a = 15.5420(10)$ Å $\alpha = 104.730(10)^\circ$ $b = 17.0260(10)$ Å $\beta = 92.640(10)^\circ$ $c = 29.1230(10)$ Å $\gamma = 115.2800(10)^\circ$
Volume	6633.2(6) Å ³
Z	2
Density (calculated)	1.310 g/cm ³
Absorption coefficient	0.177 mm ⁻¹
$F(000)$	2736
Crystal size	0.25 × 0.18 × 0.28 mm
Theta range for data collection	1.76–25.08°
Index ranges	$-12 < h < 17$, $-20 < k < 20$, $-32 < l < 14$
Reflections collected	20003
Independent reflections	17412 [$R(\text{int}) = 0.0544$]
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints	17410/0/1500
/parameters	
Goodness-of-fit on F^2	0.463
Final R indices	$R_1 = 0.0534$, $wR_2 = 0.1285$
[$I > 2\sigma(I)$]	
R indices (all data)	$R1 = 0.1159$, $wR_2 = 0.1956$
Largest diff. peak and hole	0.373 and -0.234 e Å ⁻³

Table 2
Bond lengths (Å) and angles (°)

Si(1)–O(1)	1.579(2)
Si(1)–O(2)	1.639(2)
Si(2)–O(3)	1.577(2)
Si(2)–O(2)	1.644(2)
Si(3)–O(4)	1.587(2)
Si(3)–O(5)	1.639(2)
Si(4)–O(6)	1.596(2)
Si(4)–O(5)	1.632(2)
Si(5)–O(7)	1.588(2)
Si(5)–O(8)	1.638(2)
Si(6)–O(9)	1.584(2)
Si(6)–O(8)	1.651(2)
Si(7)–O(10)	1.588(2)
Si(7)–O(11)	1.649(2)
Si(8)–O(12)	1.582(2)
Si(8)–O(11)	1.649(2)
Na(1)–O(10)	2.339(2)
Na(1)–O(3)	2.337(2)
Na(1)–O(1)	2.436(2)
Na(1)–O(12)	2.454(2)
Na(1)–O(14)	2.533(2)
Na(2)–O(4)	2.303(2)
Na(2)–O(12)	2.338(2)
Na(2)–O(6)	2.356(2)
Na(2)–O(14)	2.435(2)
Na(2)–O(13)	2.574(2)
Na(3)–O(7)	2.337(2)
Na(3)–O(10)	2.346(2)
Na(3)–O(9)	2.370(2)
Na(3)–O(13)	2.468(3)
Na(3)–O(14)	2.571(2)
Na(4)–O(10)	2.239(2)
Na(4)–O(9)	2.297(2)
Na(4)–O(1)	2.322(2)
Na(4)–N(1)	2.480(3)
Na(5)–O(1)	2.263(2)
Na(5)–O(9)	2.272(2)
Na(5)–N(2)	2.428(2)
Na(5)–O(14)	2.504(2)
Na(5)–H(1H)	2.47(3)
Na(6)–O(6)	2.289(2)
Na(6)–O(7)	2.290(2)
Na(6)–O(13)	2.425(2)
Na(6)–N(3)	2.463(3)
Na(6)–N(7)	2.765(3)
Na(6)–H(2W)	2.44(3)
Na(7)–O(6)	2.248(3)
Na(7)–O(7)	2.252(2)
Na(7)–N(4)	2.463(3)
Na(7)–O(14)	2.491(2)
Na(7)–H(1H)	2.26(3)
Na(8)–O(3)	2.259(2)
Na(8)–O(12)	2.295(2)
Na(8)–O(4)	2.304(2)
Na(8)–N(5)	2.493(2)
Na(9)–O(4)	2.262(2)
Na(9)–O(3)	2.290(2)
Na(9)–N(6)	2.501(3)
Na(9)–O(14)	2.545(2)
O(13)–H(1W)	0.93(3)
O(13)–H(2W)	0.75(4)
O(14)–H(1H)	0.79(3)
O(1)–Si(1)–O(2)	115.41(11)
O(3)–Si(2)–O(2)	113.58(9)

Table 2 (continued)

O(4)–Si(3)–O(5)	113.17(10)
O(6)–Si(4)–O(5)	113.38(11)
O(7)–Si(5)–O(8)	113.41(9)
O(9)–Si(6)–O(8)	113.31(10)
O(10)–Si(7)–O(11)	113.48(11)
O(12)–Si(8)–O(11)	112.36(10)
O(10)–Na(1)–O(3)	165.49(6)
O(10)–Na(1)–O(1)	87.68(7)
O(3)–Na(1)–O(1)	97.80(8)
O(10)–Na(1)–O(12)	86.78(7)
O(3)–Na(1)–O(12)	86.42(7)
O(1)–Na(1)–O(12)	172.44(8)
O(10)–Na(1)–O(14)	96.83(6)
O(3)–Na(1)–O(14)	96.36(7)
O(1)–Na(1)–O(14)	92.30(6)
O(12)–Na(1)–O(14)	93.47(7)
O(4)–Na(2)–O(12)	91.55(7)
O(4)–Na(2)–O(6)	105.98(8)
O(12)–Na(2)–O(6)	154.37(10)
O(4)–Na(2)–O(14)	95.79(8)
O(12)–Na(2)–O(14)	99.06(8)
O(6)–Na(2)–O(14)	97.62(7)
O(4)–Na(2)–O(13)	165.70(7)
O(12)–Na(2)–O(13)	75.61(7)
O(6)–Na(2)–O(13)	84.37(7)
O(14)–Na(2)–O(13)	92.49(8)
O(7)–Na(3)–O(10)	166.30(9)
O(7)–Na(3)–O(9)	104.49(7)
O(10)–Na(3)–O(9)	87.04(7)
O(7)–Na(3)–O(13)	83.69(7)
O(10)–Na(3)–O(13)	83.81(7)
O(9)–Na(3)–O(13)	167.93(8)
O(7)–Na(3)–O(14)	90.34(7)
O(10)–Na(3)–O(14)	95.64(6)
O(9)–Na(3)–O(14)	96.93(8)
O(13)–Na(3)–O(14)	91.81(8)
O(10)–Na(4)–O(9)	91.47(8)
O(10)–Na(4)–O(1)	92.98(8)
O(9)–Na(4)–O(1)	97.03(7)
O(1)–Na(5)–O(9)	99.47(7)
O(1)–Na(5)–O(14)	97.37(7)
O(9)–Na(5)–O(14)	101.48(8)
O(6)–Na(6)–O(7)	96.22(9)
O(6)–Na(6)–O(13)	89.34(7)
O(7)–Na(6)–O(13)	85.67(8)
O(6)–Na(7)–O(7)	98.47(9)
O(6)–Na(7)–O(14)	98.97(7)
O(7)–Na(7)–O(14)	94.43(7)
O(3)–Na(8)–O(12)	92.20(8)
O(3)–Na(8)–O(4)	92.87(7)
O(12)–Na(8)–O(4)	92.63(7)
O(4)–Na(9)–O(3)	93.18(7)
O(4)–Na(9)–O(14)	93.85(8)
O(3)–Na(9)–O(14)	97.28(7)
Si(1)–O(2)–Si(2)	144.18(14)
Na(8)–O(3)–Na(9)	87.19(8)
Na(8)–O(3)–Na(1)	92.42(8)
Na(9)–O(3)–Na(1)	87.88(6)
Na(9)–O(4)–Na(2)	89.00(8)
Na(9)–O(4)–Na(8)	86.75(8)
Na(2)–O(4)–Na(8)	88.15(7)
Si(4)–O(5)–Si(3)	151.7(2)
Na(7)–O(6)–Na(6)	82.46(8)
Na(7)–O(6)–Na(2)	84.93(9)
Na(6)–O(6)–Na(2)	97.20(9)

Table 2 (continued).

Na(7)–O(7)–Na(6)	82.36(8)
Na(7)–O(7)–Na(3)	92.62(7)
Ma(6)–O(7)–Na(3)	98.77(7)
Si(5)–O(8)–Si(6)	148.84(10)
Na(5)–O(9)–Na(4)	81.90(6)
Na(5)–O(9)–Na(3)	84.66(7)
Na(4)–O(9)–Na(3)	89.36(6)
Na(4)–O(10)–Na(1)	91.83(8)
Na(4)–O(10)–Na(3)	91.40(6)
Na(1)–O(10)–Na(3)	88.14(7)
Si(8)–O(11)–Si(7)	135.52(14)
Na(8)–O(12)–Na(2)	87.52(7)
Na(8)–O(12)–Na(1)	88.59(8)
Na(2)–O(12)–Na(1)	85.43(6)
Na(6)–O(13)–Na(3)	91.75(7)
Ma(6)–O(13)–Na(2)	88.34(8)
Na(3)–O(13)–Na(2)	87.45(8)
Na(6)–O(13)–H(1W)	153(2)
Na(3)–O(13)–H(1W)	93(2)
Na(2)–O(13)–H(1W)	65(2)
Na(6)–O(13)–H(2W)	83(2)
Na(3)–O(13)–H(2W)	120(3)
Na(2)–O(13)–H(2W)	151(3)
H(1W)–O(13)–H(2W)	118(3)
Na(2)–O(14)–Na(7)	78.29(7)
Na(2)–O(14)–Na(5)	157.94(9)
Na(7)–O(14)–Na(5)	113.93(6)
Na(2)–O(14)–Na(9)	79.95(6)
Na(7)–O(14)–Na(9)	115.37(8)
Na(5)–O(14)–Na(9)	108.54(8)
Na(2)–O(14)–Na(1)	81.74(6)
Na(7)–O(14)–Na(1)	152.92(10)
Na(5)–O(14)–Na(1)	80.22(6)
Na(9)–O(14)–Na(1)	78.44(5)
Na(2)–O(14)–Na(3)	88.24(7)
Na(7)–O(14)–Na(3)	81.92(6)
Na(5)–O(14)–Na(3)	76.06(6)
Na(9)–O(14)–Na(3)	156.10(7)
Na(1)–O(14)–Na(3)	79.35(6)
Na(2)–O(14)–H(1H)	124(3)
Na(7)–O(14)–H(1H)	64(2)
Na(5)–O(14)–H(1H)	79(3)
Na(9)–O(14)–H(1H)	80(2)
Na(1)–O(14)–H(1H)	143(2)
Na(3)–O(14)–H(1H)	123(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+1, -z$; #2 $-x+1, -y+1, -z+1$.

4.2. Preparation of $[O(Ph_2SiONa)_2]_4 \cdot (NaOH) \cdot (H_2O) \cdot (7pyridine)] \cdot (pyridine) \cdot (toluene)$ (2)

A solution of (1) (from $O(Ph_2SiOH)_2$ (5 g, 12 mmol)) and sodium dispersion (0.55 g, 24 mmol) in toluene/pyridine, was cooled in a sealed flask under air at -25°C . A colourless crystalline solid (2) (0.84 g, 10.83% based on available $O(Ph_2SiOH)_2$) was slowly deposited over a period of 3 weeks. The solid when isolated was stored under nitrogen. M.p. $91\text{--}94^\circ\text{C}$ (looses solvent).

^1H NMR (250 MHz C_6D_6 , 298 K): δ 8.25(m), 7.9(m), 7.70(m), 7.20(m), 6.60(m), 2.17(s); ^{29}Si NMR (toluene- d_8 , 297 K) δ 42.13(s); ^{23}Na NMR (toluene- d_8 ,

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Occupancy
Si(1)	7744(1)	−2125(1)	3204(1)	32(1)	
Si(2)	7057(1)	−3033(1)	2091(1)	33(1)	
Si(3)	8367(1)	−534(1)	830(1)	30(1)	
Si(4)	8881(1)	1562(1)	1202(1)	37(1)	
Si(5)	9762(1)	3275(1)	3474(1)	32(1)	
Si(6)	9220(1)	2059(1)	4179(1)	32(1)	
Si(7)	5446(1)	−111(1)	2987(1)	35(1)	
Si(8)	5108(1)	−874(1)	1890(1)	34(1)	
Na(1)	6995(1)	−1005(1)	2540(1)	33(1)	
Na(2)	7688(1)	255(1)	1827(1)	40(1)	
Na(3)	7944(1)	1185(1)	3068(1)	35(1)	
Na(4)	7145(1)	−224(1)	3712(1)	35(1)	
Na(5)	8982(1)	97(1)	3329(1)	40(1)	
Na(6)	8364(1)	2571(1)	2310(1)	43(1)	
Na(7)	9691(1)	1751(1)	2421(1)	46(1)	
Na(8)	6417(1)	−1902(1)	1350(1)	35(1)	
Na(9)	8549(1)	−1132(1)	1874(1)	42(1)	
O(1)	7646(1)	−1224(1)	3248(1)	32(1)	
O(2)	7554(1)	−2786(1)	2653(1)	34(1)	
O(3)	7982(1)	−2184(1)	1956(1)	34(1)	
O(4)	7894(1)	−848(1)	1265(1)	33(1)	
O(5)	8664(1)	536(1)	884(1)	39(1)	
O(6)	8815(1)	1663(1)	1757(1)	48(1)	
O(7)	9148(1)	2523(1)	2979(1)	34(1)	
O(8)	9777(1)	2852(1)	3920(1)	35(1)	
O(9)	8540(1)	1092(1)	3806(1)	33(1)	
O(10)	6488(1)	−61(1)	3064(1)	30(1)	
O(11)	5017(1)	−302(1)	2420(1)	38(1)	
O(12)	6153(1)	−807(1)	1878(1)	33(1)	
O(13)	7008(1)	1217(1)	2371(1)	46(1)	
O(14)	8625(1)	239(1)	2515(1)	31(1)	
C(1)	6888(1)	−2893(1)	3530(1)	36(1)	
C(2)	6216(1)	−2680(1)	3758(1)	49(1)	
C(3)	5584(1)	−3269(2)	3979(1)	58(1)	
C(4)	5623(2)	−4072(1)	3972(1)	54(1)	
C(5)	6295(2)	−4286(1)	3743(1)	53(1)	
C(6)	6927(1)	−3697(1)	3522(1)	48(1)	
C(7)	9002(1)	−1889(1)	3477(1)	33(1)	
C(8)	9282(1)	−1518(1)	3975(1)	48(1)	
C(9)	10164(1)	−1390(2)	4196(1)	61(1)	
C(10)	10766(1)	−1634(2)	3918(1)	62(1)	
C(11)	10486(1)	−2005(2)	3420(1)	66(1)	
C(12)	9604(1)	−2132(1)	3200(1)	49(1)	
C(13)	7735(1)	−3555(1)	1690(1)	34(1)	
C(14)	7863(1)	−3398(1)	1246(1)	44(1)	
C(15)	8327(2)	−3797(2)	943(1)	55(1)	
C(16)	8662(2)	−4353(2)	1084(1)	71(1)	
C(17)	8533(2)	−4510(1)	1527(1)	75(1)	
C(18)	8070(1)	−4111(1)	1830(1)	55(1)	
C(19)	5790(1)	−4031(1)	1996(1)	38(1)	
C(20)	5347(1)	−4577(1)	1526(1)	56(1)	
C(21)	4476(1)	−5361(1)	1442(1)	77(2)	
C(22)	4049(1)	−5598(1)	1827(1)	56(1)	
C(23)	4492(1)	−5551(1)	2297(1)	63(1)	
C(24)	5362(1)	−4267(1)	2382(1)	53(1)	
C(25)	7487(1)	−1236(1)	231(1)	38(1)	
C(26)	7742(1)	−1710(1)	−156(1)	49(1)	
C(27)	7087(2)	−2216(2)	−586(1)	70(1)	
C(28)	6177(2)	−2248(2)	−629(1)	99(2)	
C(29)	5922(1)	−1774(2)	−242(1)	147(3)	
C(3)	6578(1)	−1268(2)	189(1)	92(2)	

Table 3 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occupancy
C(31)	9499(1)	−695(1)	761(1)	33(1)	
C(32)	9513(1)	−1451(1)	855(1)	49(1)	
C(33)	10320(1)	−1601(1)	807(1)	56(1)	
C(34)	11114(1)	−995(2)	666(1)	55(1)	
C(35)	11101(1)	−239(1)	572(1)	53(1)	
C(36)	10293(1)	−89(1)	620(1)	40(1)	
C(37)	8009(2)	1832(2)	892(2)	62(1)	
C(38)	8106(3)	2651(2)	915(2)	129(2)	
C(39)	7508(3)	2912(2)	700(2)	85(1)	
C(40)	6888(4)	2286(4)	215(3)	69(2)	0.47197
C(40)	6681(4)	2389(4)	648(3)	67(2)	0.52803
C(41)	7010(4)	1534(4)	25(3)	55(2)	0.46832
C(41)	6363(4)	1570(4)	746(3)	68(3)	0.53168
C(42)	7529(4)	1270(4)	302(2)	43(2)	0.45220
C(42)	7042(4)	1339(4)	926(3)	62(2)	0.54780
C(43)	10108(1)	2377(1)	1104(1)	36(1)	
C(44)	10798(1)	3045(1)	1497(1)	45(1)	
C(45)	11639(1)	3713(1)	1422(1)	62(1)	
C(46)	11791(1)	3714(1)	956(1)	70(1)	
C(47)	11101(2)	3047(1)	564(1)	60(1)	
C(48)	10260(1)	2378(1)	638(1)	43(1)	
C(49)	11091(1)	3933(1)	3427(1)	34(1)	
C(50)	11306(1)	4261(1)	3024(1)	44(1)	
C(51)	12264(1)	4770(1)	2999(1)	53(1)	
C(52)	13005(1)	4950(1)	3357(1)	54(1)	
C(53)	12790(1)	4622(1)	3749(1)	59(1)	
C(54)	11832(1)	4113(1)	3784(1)	47(1)	
C(55)	9309(1)	4158(1)	3679(1)	35(1)	
C(56)	8320(1)	3879(1)	3637(1)	49(1)	
C(57)	7979(1)	4518(2)	3791(1)	63(1)	
C(58)	8627(2)	5436(1)	3987(1)	66(1)	
C(59)	9616(2)	5715(1)	4029(1)	61(1)	
C(60)	9957(1)	5076(1)	3875(1)	48(1)	
C(61)	10245(1)	2027(1)	4553(1)	32(1)	
C(62)	11009(1)	2839(1)	4838(1)	43(1)	
C(63)	11789(1)	2827(1)	5084(1)	51(1)	
C(64)	11805(1)	2003(2)	5045(1)	54(1)	
C(65)	11041(2)	1192(1)	4760(1)	50(1)	
C(66)	10261(1)	1203(1)	4514(1)	45(1)	
C(67)	8581(1)	2539(1)	4628(1)	35(1)	
C(68)	8730(1)	3435(1)	4730(1)	46(1)	
C(69)	8279(2)	3767(1)	5075(1)	66(1)	
C(70)	7678(2)	3202(2)	5317(1)	70(1)	
C(71)	7529(1)	2306(2)	5215(1)	69(2)	
C(72)	7980(1)	1974(1)	4870(1)	58(1)	
C(73)	5416(1)	991(1)	3307(1)	42(1)	
C(74)	4801(1)	1256(1)	3101(1)	56(1)	
C(75)	4802(2)	2079(1)	3330(1)	70(1)	
C(76)	5418(2)	2637(1)	3767(1)	68(1)	
C(77)	6033(2)	2373(1)	3973(1)	69(1)	
C(78)	6032(1)	1550(1)	3744(1)	58(1)	
C(79)	4542(1)	−1066(1)	3201(1)	42(1)	
C(80)	4652(2)	−1850(1)	3150(1)	63(1)	
C(81)	3983(2)	−2565(1)	3289(1)	87(2)	
C(82)	3204(2)	−2496(2)	3478(1)	106(2)	
C(83)	3095(2)	−1711(2)	3529(1)	114(2)	
C(84)	3763(1)	−996(2)	3390(1)	76(1)	
C(85)	4752(2)	−390(2)	1454(1)	53(1)	
C(86)	4224(2)	95(2)	1525(1)	54(1)	
C(87)	3924(2)	411(3)	1187(2)	84(2)	
C(88)	4462(5)	566(4)	815(3)	77(3)	0.44634
C(88)	3740(5)	−233(5)	690(3)	79(3)	0.55366
C(89)	5203(6)	339(5)	755(3)	93(3)	0.52023
C(89)	4073(6)	−842(5)	575(3)	76(3)	0.47977

Table 3 (continued).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occupancy
C(90)	5383(4)	−142(4)	1980(2)	51(2)	0.50589
C(90)	4551(5)	−986(4)	962(3)	70(3)	0.49411
C(91)	4123(1)	−2084(1)	1746(1)	67(1)	
C(92)	4316(2)	−2732(1)	1874(1)	88(2)	
C(93)	3584(2)	−3614(1)	1785(2)	173(3)	
C(94)	2658(2)	−3848(1)	1566(2)	225(4)	
C(95)	2464(1)	−3199(2)	1438(2)	256(5)	
C(96)	3197(1)	−2317(2)	1528(1)	134(3)	
N(1)	6481(2)	−536(2)	3330(1)	44(1)	
C(97)	5567(2)	−802(3)	4505(1)	79(2)	
C(98)	5270(2)	−974(3)	4923(2)	99(2)	
C(99)	5917(3)	−895(3)	5279(2)	82(1)	
C(100)	6840(2)	−604(2)	5226(1)	75(1)	
C(101)	7084(2)	−446(2)	4802(1)	57(1)	
N(2)	10721(2)	772(1)	3366(1)	47(1)	
C(102)	11249(2)	1675(2)	3559(1)	54(1)	
C(103)	12214(2)	2094(2)	3767(1)	65(1)	
C(104)	12657(2)	1546(3)	3775(2)	78(2)	
C(105)	12134(2)	637(3)	3585(2)	77(2)	
C(106)	11180(2)	267(2)	3388(1)	64(1)	
N(3)	9121(2)	4158(2)	2288(1)	57(1)	
C(107)	9122(2)	4812(2)	2661(1)	69(1)	
C(108)	9814(3)	5707(2)	2797(2)	99(2)	
C(109)	10528(3)	5931(3)	2553(2)	107(2)	
C(110)	10559(3)	5304(3)	2156(2)	106(2)	
C(111)	9817(2)	4416(2)	2042(1)	75(1)	
N(4)	11325(2)	1991(2)	2285(1)	48(1)	
C(112)	11431(2)	1583(2)	1850(1)	55(1)	
C(113)	12309(2)	1674(2)	1733(1)	70(1)	
C(114)	13108(2)	2225(2)	2082(2)	78(2)	
C(115)	13020(2)	2661(2)	2520(1)	60(1)	
C(116)	12119(2)	2532(2)	2601(1)	51(1)	
N(5)	5256(2)	−3180(2)	648(1)	62(1)	
C(117)	4317(2)	−3509(3)	600(2)	99(2)	
C(118)	3679(3)	−4117(3)	176(2)	135(3)	
C(119)	4018(4)	−4394(4)	−195(2)	187(3)	
C(120)	4986(5)	−4090(4)	−152(2)	237(4)	
C(121)	5565(3)	−3449(4)	280(2)	160(3)	
N(6)	10129(2)	−1139(2)	2072(1)	50(1)	
C(122)	10932(2)	−350(2)	2193(2)	77(2)	
C(123)	11842(3)	−283(2)	2241(2)	93(2)	
C(124)	11964(2)	−1044(2)	2199(2)	74(2)	
C(125)	11163(2)	−1853(2)	2074(2)	77(2)	
C(126)	10261(2)	−1871(2)	2018(1)	62(1)	
N(7)	6625(2)	2655(2)	2276(1)	77(1)	
C(127)	6401(2)	3142(3)	2613(2)	95(2)	
C(128)	6113(2)	3769(3)	2525(2)	137(2)	
C(129)	6032(3)	3850(2)	2085(2)	129(3)	
C(130)	6198(3)	3312(3)	1741(2)	190(2)	
C(131)	6516(3)	2746(3)	1859(2)	207(2)	
C(132)	10746(3)	5076(3)	325(2)	143(3)	
C(133)	9915(3)	4264(3)	152(2)	138(2)	
C(134)	10821(3)	5812(3)	156(2)	139(3)	
C(135)	11673(6)	6881(6)	484(4)	110(3)	
N(8)	4116(3)	4576(5)	4887(1)	232(4)	
C(136)	4150(7)	5464(5)	5054(2)	254(6)	
C(137)	4671(6)	4033(5)	4797(2)	233(5)	

300 K): δ 10.1 (br s). Found: C 65.17, H 5.15, N, 5.14. Calculated for C₁₄₃H₁₃₁N₈Na₉O₁₄Si₈: C 65.86, H 5.07, N 4.84.

Crystal data for $C_{143}H_{131}N_8Na_9O_{14}Si_8$ (dimension: $0.3 \times 0.2 \times 0.2 \text{ mm}^3$): $M = 2585.19$, triclinic, space group $P-1$ (no. 2) with $a = 15.542(1)$, $b = 17.026(1)$, $c = 29.123(1) \text{ \AA}$, $\alpha = 104.73(1)$, $\beta = 92.64(1)$, $\gamma = 115.28(1)^\circ$, $U = 6633.2(6) \text{ \AA}^3$, $Z = 2$, $D_c = 1.310 \text{ g cm}^{-3}$, $F(000) = 2736$, $\mu(\text{Mo-K}\alpha) = 0.175 \text{ mm}^{-1}$, $T = 150 \text{ K}$, 20003 reflections were measured with FAST [19] area detector using Mo-K α ($\lambda = 0.71069 \text{ \AA}$) radiation. Data were uncorrected for absorption. 17412 independent reflections were measured, $R_{\text{int}} = 0.054$ ($1.76^\circ < \theta < 25.08^\circ$). The structure was solved by direct methods and difference Fourier technique (SHELXS-86) [20]. Refinement was carried out with full-matrix least-squares on F^2 (SHELXL-93) [21]. $R = \sum |F_o - F_c| / \sum F_o = 0.0534$ [4966 reflections with $I > 2\sigma(I)$]. $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2} = 0.1956$, $w = 1 / [\sigma^2(F_o^2) + (0.10P)^2 + 0.00P]$ where $P = (F_o^2 + 2F_c^2) / 3$, and residual electron density $0.373 / -0.234 \text{ e \AA}^{-3}$. Hydrogen atoms on H_2O and HO^- groups were located in the difference map and their position successfully refined. All other hydrogen atoms were geometrically ideally positioned and refined according to the riding model using fixed isotropic displacement parameters. Two of the phenyl rings ($C_{37}-C_{42}$) and ($C_{85}-C_{90}$) were modelled for disorder. The occupancies for each disordered atom pair were refined separately and then fixed. In these cases the hydrogen atoms were omitted. Diagrams were drawn with PLATON [22]. Crystal data are given in Table 1, selected bond distances and angles in Table 2 and fractional atomic coordinates in Table 3. Supplementary data (atomic coordinates, bond lengths and angles and thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank EPSRC and Shell Research Ltd for a Quota/CASE to SAAS. We gratefully acknowledge Dr. Andy Quick for his advice and help with refinement of the structure and Professor M.B. Hursthouse (University of Wales, Cardiff), director of the EPSRC Crystallography Service, is thanked for measuring the X-ray data.

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