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A new approach to the synthesis of cage-like metallasiloxanes

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Abstract

A new approach to the synthesis of cage-like metallasiloxanes has been proposed. Copper-containing metallasiloxanes $\{Na_4[(RSiO_2)_{12}Cu_4](R'OH)_n\}$ (**1a**, R = Ph, R′ = *n*-Bu; **1b**, R = Ph, R′ = Me; **2**, R = Vi, R′ = Me) were prepared from $PhSi(OR)_3 \cdot$(R = *n*-Bu, Me) and $ViSi(OMe)_3$, respectively. Compound **2** was characterized by X-ray single structure analysis. The structures of compounds **1a**,**b** were deduced by their follow up reactions with Me_3SiCl. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cage-like metallasiloxanes; Alkoxysilanes trimethylsilylation; X-ray single structure analysis

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1. Introduction

Recently a new class of cage-like metallasiloxanes (involving alkaline metals, Mn, Co, Ni, Cu and trivalent lanthanide metals) was obtained and structurally characterized [1,2]. For their synthesis the exchange reaction of the corresponding metal chloride with the alkaline metal organosiloxanolates was used. Sodium or potassium organosiloxanolates were prepared in situ via alkaline splitting of oligoorganosilsesquioxanes of low molecular weight in *n*-butanol as a solvent.

We have now extended our studies to the synthesis of cage-like metallasiloxanes and report here on the new route for their preparation from individual organoalkoxysilanes. The example of copper/sodium containing cage-like metallasiloxanes (involving alkaline metal and copper). $Na_4[(RSiO_2)_{12}Cu_4](R'OH)_n\}$ (R = Ph, Vi; R′ = *n*-Bu, Me, Et) is described herein.

2. Results and discussion

2.1. Synthesis

Earlier for the preparation of individual crystalline metallaorganosiloxanes we used oligoorganolsilsesquioxane resin as a starting reagent according to the following scheme:

$$m/n[RSiO_{1.5}]_n + m\,NaOH \overset{n-\mathrm{BuOH}}{\rightarrow} [RSi(O)ONa]_m$$

$$x/m[RSi(O)ONa]_m + MCl_x \underset{-x\mathrm{NaCl}}{\overset{m-\mathrm{BuOH}}{\rightarrow}} [(RSiO_{1.5})_x(M_{2/x}O_{x/2})]$$

Oligoorganosilsesquioxane resin was treated with an equimolecular amount of NaOH in *n*-butanol and then the mixture obtained was subsequently treated with the metal chlorides to yield the products [1,2]. The mechanism of the formation of cage-like metallasiloxanes is not well understood. It has been suggested [3] that this formation goes via intermediate [RSiOONa] species that exist in an associative form in n-butanol solution:

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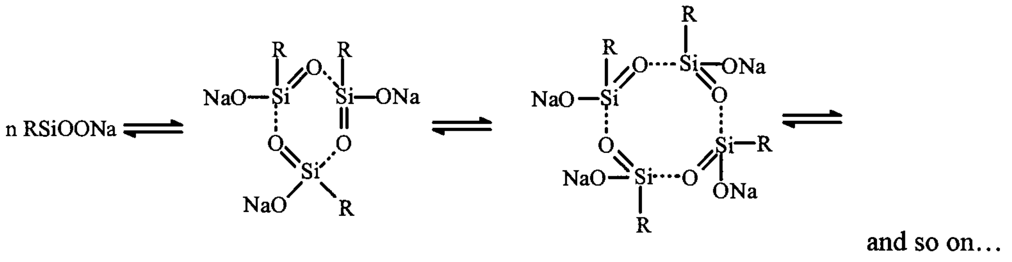
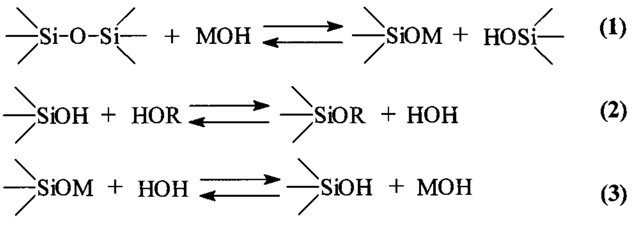
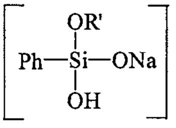


On the basis of new experimental data we would like to present now another view on this matter. Since the reaction of alkaline splitting of silsesquioxane resin is performed in an alcohol solvent it is reasonable to envision at least three reactions which can take place in the process [4]:



and to assume that as the result of these possible reactions and a rapid proton-cation exchange between OH- and NaO -groups [5] an equilibrium reacting unit in alcohol solution can be presented as:



(R'=alkyl, H).

Such labile units generated in situ can easily undergo spontaneous oligocyclization in the presence of transition metal cations that play the role of template centers, yielding cage-like metallasiloxanes which are based on one or two stereoregular siloxanolate macrocycles $[RSi(O-)O]_n$ with $n = 6$, 8, 12 [1].

In order to check up this assumption we decided to study the possibility of making copper/sodium-containing metallasiloxanes from various organoalkoxysilanes: $PhSi(OBu^n)_3$, $PhSi(OMe)_3$ and $ViSi(OMe)_3$ in the presence of some amount of water according to the following scheme:

$$RSi(OR')_3 + NaOH + H_2O$$

$$\rightarrow [(R)(OR')Si(OH)(ONa)] \overset{CuCl_2}{\rightarrow} CuCl_2\ \underset{1a,b;2}{\{Na_4[RSiO_2]_{12}Cu_4\}(L)_x}$$

$$(L = HOBu,\ HOEt,\ HOMe,\ H_2O)$$

where $R = Ph$, $R' = Bu^n$ (**1a**); $R = Ph$, $R' = Me$ (**1b**); $R = Vi$, $R'Me$ (**2**).

The crystalline copper/sodium-organosiloxanes $\{Na_4\{[RSiO_2]_{12}Cu_4\} \cdot (L)_x$ (**1a**,**b**; **2**) were obtained in good yields. The amount of water molecules used depended on the substituent attached to silicon atom: for $PhSi(OR')_3$ ($R' = n$-Bu, Me) water was used in equimoleqular ratio; in the case of $ViSi(OMe)_3$ nine molecules of water per one molecule of $ViSi(OMe)_3$ were used.

Copper/sodium-vinylsiloxane $\{Na_4[ViSiO_2]_{12}Cu_4\} \cdot 4n$-BuOH (**2**) was obtained for the first time and according to the X-ray single structure analysis its molecule has the same framework structure (Fig. 1) as described earlier $\{K_4[(ViSiO_2)_{12}Cu_4]\}(6n$-BuOH) (**3**) and $\{Na_4[(PhSiO_2)_{12}Cu_4]\}(8n$-BuOH) (**4**) ([1]c).

We postulated that the framework structures of copper/sodium-phenylsiloxane molecules **1a** and **1b** are the same as the framework structure of copper/sodium-phenylsiloxane **4** obtained earlier ([1]c).

Evidence to support this were obtained from elemental analysis and from the reaction of **1a** and **1b** with trimethylchlorosilane according to the following scheme:

$$\underset{\mathbf{1a,b}}{\left\{Na_4[RSiO_2]_{12}Cu_4\right\}} \cdot (L)_x$$

$$+ Me_3SiCl^{Py} \overset{benzene}{\rightarrow} \underset{\mathbf{5}}{[PhSi(O)(OSiMe_3)]_{12}}$$

The stereoregular tris-*cis*-tris-*trans*-dodecaphenylcyclododecasiloxanolate $[PhSi(O)O^-]_{12-}$ the main struc-

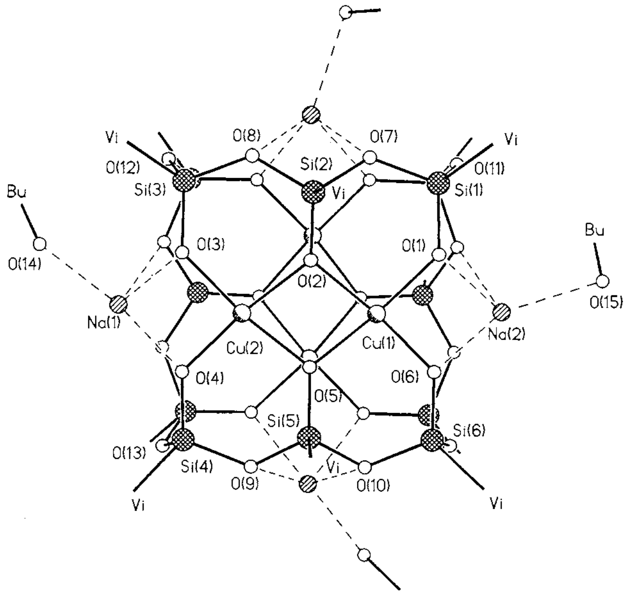


Fig. 1. The general view and numbering scheme of complexes **2**. The Vi and Bu groups are omitted for clarity. The Na–O bonds are shown by dashed lines.

Table 1
Crystal data and details of the X-ray experiments for 2

Formula weight	$C_{40}H_{72}Cu_4Na_4O_{28}Si_{12}$
Molecular weight	1684.18
Crystal color, habit	Blue prism
Crystal size (mm)	0.10 × 0.20 × 0.20
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell constants	
a (Å)	15.471(7)
b (Å)	30.344(13)
c (Å)	16.162(9)
β (°)	100.27(2)
V (Å^3)	7466(6)
Z	4
$D_{calc.}$ (g cm^{-3})	1.498
Diffractometer	Siemens P3/PC
Temperature (K)	153
Radiation (Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$)
Scan mode	θ-2θ
$2\theta_{max}$ (°)	54
Total unique reflections collected	7010
Absorption coefficient, μ(Mo–K$_\alpha$) (mm^{-1})	1.410
R_1 (on F for reflections with $I > 2\sigma > (I)$)	0.0771 (4215)
wR_2 (on F^2 for all reflections)	0.1853 (6945)
Largest difference peak and hole (e Å^{-3})	1.628, −1.277

tural forming fragment of **1a**, **b**-was isolated as trimethylsiloxy derivative **5** (according to the method of trimethylsilylation [6]).

2.2. X-ray structure

To determine the exact molecular structures, single-crystal X-ray analysis was undertaken. The formula of this complex **2** was revealed to be $Na_4\{[ViSiO_2]_{12}Cu_4\} \cdot 4n$-BuOH. The X-ray structure of **2** with the atomic numbering schemes are presented in Fig. 1 (the basic geometric parameters of the molecule are given in Tables 1–3, and the selected bond lengths and bond angles are given in Table 3.

The bond lengths and angles in **2** (Table 3) are very similar to the corresponding ones in the $Na_4\{[PhSiO_2]_{12}Cu_4\} \cdot 8n$-BuOH (**4**) and $K_4\{[ViSiO_2]_{12}Cu_4\} \cdot 6n$-BuOH (**3**) complexes ([1]c). It is interesting to mention, that complexes **3** and **4** have $\bar{4}$ and 222 crystallographic symmetry, in contrast to **2** which has crystallographic C_2 axis through the O(11) and O(13) oxygen atoms. So, the exchange of the potassium ion in **3** by sodium one in **2** causes the lowering of the complex symmetry.

In complex **2** the cyclododecasiloxanolate ligand is characterized by tris*(cis)*-*trans*-tris*(cis)*-*trans*-tris*(cis)*-*trans*-tris*(cis)* configuration. In further discussion the oxygen atoms of the siloxanolate ligand bound to the metal atoms will be indicated as O_m, whereas the others belonging to the ligand will be written as O_c. The Cu atoms in **2** are characterized by square planar coordination. The Cu–O_m distances vary in the range of 1.888(5)–1.947(6)Å, which is in aggreement with the sum of the ionic radii of O^{2-} and square planar Cu^{2+} (1.93 Å) [7]. The angles at the bridging O_m atoms (Cu(1)–O(2)–Cu(2) and Cu(1)–O(5)–Cu(2)) 101.3(2) and 101.5(2)° are similar to the corresponding values in **3** and **4** (101.7 and 101.3°, respectively). The Cu_2O_6 moieties have 'staggered' orientation (the Cu atoms are projected to O_m ($-x$, y, $-z + 1/2$) and vice versa).

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **2**

Atom	*x*	*y*	*z*	U_{eq}
Cu(1)	782(1)	3888(1)	1641(1)	37(1)
Cu(2)	1310(1)	3180(1)	2934(1)	38(1)
Si(1)	937(2)	4881(1)	2371(1)	38(1)
Si(2)	1903(2)	4182(1)	3403(1)	38(1)
Si(3)	1969(2)	3555(1)	4818(1)	36(1)
Si(4)	871(1)	2187(1)	2253(1)	31(1)
Si(5)	842(1)	2898(1)	1024(1)	30(1)
Si(6)	−138(2)	3520(1)	−174(1)	37(1)
Na(1)	1101(2)	2516(1)	4341(2)	37(1)
Na(2)	−564(3)	4547(1)	506(3)	63(1)
O(1)	811(4)	4522(2)	1636(3)	41(1)
O(2)	1364(6)	3816(2)	2802(3)	67(2)
O(3)	1825(3)	3182(2)	4105(3)	31(1)
O(4)	1263(3)	2552(2)	2933(3)	31(1)
O(5)	785(5)	3250(2)	1759(3)	54(2)
O(6)	232(4)	3888(2)	501(3)	50(2)
O(7)	1375(4)	4650(2)	3276(3)	38(1)
O(8)	1945(4)	4047(2)	4382(3)	42(1)
O(9)	558(3)	2414(2)	1312(3)	33(1)
O(10)	104(3)	3018(2)	204(3)	31(1)
O(11)	0	5087(2)	2500	41(2)
O(12)	1209(4)	3547(2)	5392(3)	44(1)
O(13)	0	1955(2)	2500	32(2)
O(14)	1843(3)	2428(2)	5688(3)	37(1)
O(15)	−949(6)	5267(3)	−165(5)	124(5)
C(1)	1646(9)	5338(3)	2166(7)	70(3)
C(2)	1531(9)	5740(4)	2235(8)	80(3)
C(3)	3013(8)	4261(4)	3169(7)	75(3)
C(4)	3314(13)	4125(7)	2533(13)	147(8)
C(5)	3012(6)	3490(3)	5553(5)	52(2)
C(6)	3727(8)	3724(4)	5591(7)	79(3)
C(7)	1640(6)	1741(3)	2119(5)	45(2)
C(8)	1894(9)	1635(4)	1435(8)	88(4)
C(9)	1937(7)	2890(5)	746(10)	98(5)
C(10)	2620(10)	2980(8)	1008(14)	184(12)
C(11)	293(6)	3566(3)	−1162(5)	47(2)
C(12)	721(7)	3265(4)	−1483(6)	60(3)
C(13)	1473(5)	2488(3)	6422(5)	41(2)
C(14)	974(6)	2081(3)	6640(6)	54(2)
C(15)	216(7)	1952(3)	5951(7)	60(3)
C(16)	−219(8)	1528(4)	6156(8)	73(3)
C(17)	−1654(8)	5446(4)	329(10)	88(4)
C(18)	−2569(14)	5359(9)	−150(18)	167(10)
C(19)	−3205(18)	5573(9)	252(24)	99(12)
C(20)*	4198(21)	5413(13)	−162(38)	162(23)
C(19′)*	−3193(39)	5102(25)	−205(39)	224(30)
C(20′)**	4041(26)	5145(19)	−694(39)	182(24)

*S.O.F., 0.55; ** S.O.F., 0.45.

Table 3
Selected bond lengths (A) and angles (°) in **2**

Bond lengths			
Cu(1)–O(6)	1.888(5)	Si(4)–O(9)	1.661(5)
Cu(1)–O(1)	1.924(5)	Si(5)–O(5)	1.611(6)
Cu(1)–O(2)	1.943(6)	Si(5)–O(9)	1.625(5)
Cu(1)–O(5)	1.946(6)	Si(5)–O(10)	1.629(5)
Cu(2)–O(4)	1.907(5)	Si(6)–O(6)	1.594(6)
Cu(2)–O(3)	1.918(5)	Si(6)–O(12)*	1.633(6)
Cu(2)–O(5)	1.939(5)	Si(6)–O(10)	1.659(5)
Cu(2)–O(2)	1.947(6)	Na(1)–O(14)	2.288(6)
Si(1)–O(1)	1.597(5)	Na(1)–O(4)	2.335(6)
Si(1)–O(11)	1.626(4)	Na(1)–O(3)	2.373(6)
Si(1)–O(7)	1.653(6)	Na(1)–O(10)*	2.612(6)
Si(2)–O(2)	1.607(6)	Na(1)–O(9)*	2.614(6)
Si(2)–O(8)	1.625(6)	Na(2)–O(6)	2.348(7)
Si(2)–O(7)	1.634(6)	Na(2)–O(15)**	2.56(1)
Si(3)–O(3)	1.603(5)	Na(2)–O(7)*	2.536(7)
Si(3)–O(12)	1.623(6)	Na(2)–O(1)	2.545(7)
Si(3)–O(8)	1.646(6)	Na(2)–O(15)	2.46(1)
Si(4)–O(4)	1.601(5)	Na(2)–O(8)*	2.653(7)
Si(4)–O(13)	1.632(4)		
Bond angles			
O(6)–Cu(1)–O(1)	90.1(2)	O(6)–Na(2)–O(15)	147.0(3)
O(6)–Cu(1)–O(2)	173.5(2)	O(15)**–Na(2)–O(15)	82.4(3)
O(1)–Cu(1)–O(2)	96.3(2)	O(7)*–Na(2)–O(15)	96.7(3)
O(6)–Cu(1)–O(5)	95.1(2)	O(1)–Na(2)–O(15)	116.6(3)
O(1)–Cu(1)–O(5)	174.7(2)	O(6)–Na(2)–O(8)*	86.7(2)
O(2)–Cu(1)–O(5)	78.5(2)	O(15)**–Na(2)–O(8)*	156.8(3)
O(4)–Cu(2)–O(3)	90.7(2)	O(7)*–Na(2)–O(8)*	60.1(2)
O(4)–Cu(2)–O(5)	95.7(2)	O(1)–Na(2)–O(8)*	121.0(2)
O(3)–Cu(2)–O(5)	173.5(2)	O(15)–Na(2)–O(8)*	113.7(3)
O(4)–Cu(2)–O(2)	173.6(2)	Si(1)–O(1)–Cu(1)	132.7(3)
O(3)–Cu(2)–O(2)	95.0(2)	Si(1)–O(1)–Na(2)	119.3(3)
O(5)–Cu(2)–O(2)	78.6(2)	Cu(1)–O(1)–Na(2)	90.9(2)
O(1)–Si(1)–O(11)	111.4(3)	Si(2)–O(2)–Cu(1)	127.4(4)
O(1)–Si(1)–O(7)	110.3(3)	Si(2)–O(2)–Cu(2)	130.3(4)
O(11)–Si(1)–O(7)	106.5(2)	Cu(1)–O(2)–Cu(2)	101.3(3)
O(2)–Si(2)–O(8)	109.9(3)	Si(3)–O(3)–Cu(2)	133.7(3)
O(2)–Si(2)–O(7)	109.3(3)	Si(3)–O(3)–Na(1)	119.7(3)
O(8)–Si(2)–O(7)	106.0(3)	Cu(2)–O(3)–Na(1)	91.7(2)
O(3)–Si(3)–O(12)	112.2(3)	Si(4)–O(4)–Cu(2)	134.5(3)
O(3)–Si(3)–O(8)	110.1 (3)	Si(4)–O(4)–Na(1)	123.0(3)
O(12)–Si(3)–O(8)	107.2(3)	Cu(2)–O(4)–Na(1)	93.2(2)
O(4)–Si(4)–O(13)	111.0(3)	Si(5)–O(5)–Cu(2)	125.5(3)
O(4)–Si(4)–O(9)	110.8(3)	Si(5)–O(5)–Cu(1)	125.9(3)
O(13)–Si(4)–O(9)	106.5(2)	Cu(2)–O(5)–Cu(1)	101.5(2)
O(5)–Si(5)–O(9)	109.6(3)	Si(6)–O(6)–Cu(1)	135.4(3)
O(5)–Si(5)–O(10)	109.3(3)	Si(6)–O(6)–Na(2)	118.3(3)
O(9)–Si(5)–O(10)	104.3(3)	Cu(1)–O(6)–Na(2)	98.1(3)
O(6)–Si(6)–O(12)*	109.8(3)	Si(2)–O(7)–Si(1)	126.6(3)
O(6)–Si(6)–O(10)	111.2(3)	Si(2)–O(7)–Na(2)*	95.7(3)
O(12)*–Si(6)–O(10)	106.2(3)	Si(1)–O(7)–Na(2)	123.9(3)
O(6)–Si(6)–C(11)	113.4(4)	Si(2)–O(8)–Si(3)	129.8(3)
O(14)–Na(1)–O(4)	144.1(2)	Si(2)–O(8)–Na(2)*	91.6(3)
O(14)–Na(1)–O(3)	94.7(2)	Si(3)–O(8)–Na(2)*	1116.4(3)
O(4)–Na(1)–O(3)	70.7(2)	Si(5)–O(9)–Si(4)	125.9(3)
O(14)–Na(1)–O(10)*	93.6(2)	Si(5)–O(9)–Na(1)*	94.2(2)
O(4)–Na(1)–O(10)*	117.0(2)	Si(4)–O(9)–Na(1)*	121.6(3)
O(3)–Na(1)–O(10)	86.0(2)	Si(5)–O(10)–Si(6)	125.7(3)
O(14)–Na(1)–O(9)*	131.3(2)	Si(5)–O(10)–Na(1)*	94.2(2)
O(4)–Na(1)–O(9)*	83.1(2)	Si(6)–O(10)–Na(1)*	120.9(3)
O(3)–Na(1)–O(9)*	119.6(2)	Si(1)*–O(11)–Si(1)	134.7(5)
O(10)*–Na(1)–O(9)*	58.9(2)	Si(3)–O(12)–Si(6)*	133.4(4)
O(6)–Na(2)–O(15)	71.8(3)	Si(4)*–O(13)–Si(4)	128.8(4)
O(6)–Na(2)–O(7)*	116.2(2)	C(13)–O(14)–Na(1)	124.9(5)
O(15)**–Na(2)–O(7)*	137.5(3)	C(17)–O(15)–Na(2)**	141.5(7)
O(6)–Na(2)–O(1)	66.8(2)	C(17)–O(15)–Na(2)	102.7(8)
O(15)**–Na(2)–O(1)	58.8(2)	Na(2)**–O(15)–Na(2)	97.6(3)
O(7)*–Na(2)–O(1)	85.0(2)		

Table 3 (Continued)

*, ** Atoms generated from the reference atoms by the −x, y, −z+1/2 and −x, −y+1, −z symmetry transformations.

The Cu–Cu distance in **2** (3.008(2) Å) is equal to the corresponding values in **3** and **4** (3.02, 3.06 Å), whereas the distances between the dimeric moieties are slightly shortened (3.371 and 3.597(5) Å for Cu(1) and to Cu(2), respectively), in comparison with 3.899(3) and 3.386(3) Å for **3**, **4**. In all cases, the distance between the dimeric units are such as to exclude the apical coordination of a Cu atom by an O_m atom of the neighboring Cu_2O_6 unit.

The bond angles OSiO in **2** vary in the range 106.0(3)–113.4(4)° and are close to the value of the ideal tetrahedral angle. The Si–O_c–Si vary in the widened range 125.7(4)–134.7(5)° which is usually observed for cyclic siloxanes [8].

The sodium ions in structure **2** are characterized by the coordination number 5 for Na(1) and 6 for Na(2). The Na–O bond lengths vary in the range 2.46(1)–2.288(6) Å.

The analysis of the molecular packing reveals that in structure **2** due to the Na(2)–O(15) (−x, −y+1, −z) bond, complexes form zig-zag chains directed along OX axes (Fig. 2). The H-bonds of the Bu–OH alcohol oxygen atoms with the O_c ones link these chains in the three-dimensional framework.

3. Experimental

The 1H- and 29Si-NMR spectra were recorded with a Bruker WP-SY200 spectrometer (200.13 MHz for 1H, 39.76 MHz for 29Si) at 20°C in CCl_4 solution with TMS as an internal reference standard.

GPC was performed on a Waters instrument with an M-600 pump and an M-484 UV-detector at wavelength 254 nm on columns U-Styragel 500, 1000 Å, using a Maxima information processing computer system.

3.1. *X-ray data collection, structure determination, and refinement for **2***

Single crystal of **2** was slowly grown from solution in *n*-butanol. Accurate unit cell parameters and orientation matrices were obtained by least-squares refinement of carefully centered 24 reflections in the $23° \leq \theta \leq 27°$ ranges. Two standard reflections were monitored every 98 reflections for **2** and showed no significant variations in all cases. Data were corrected for Lorentz and polarization effects. A carefully chosen, rather small, well formed and essentially isometric single-crystal sample, the quality of the obtained results, and the relatively low absorption coefficient value justified no need for absorption corrections.

The structure was solved by direct methods and subsequent difference Fourier maps. The difference Fourier synthesis for **2** revealed additional peaks which were interpreted as a disorder of the terminal carbon atoms of the OBu group. The occupancies of the two positions labeled C(19), C(20) and C(19′), C(20′) refined to 0.55 and 0.45, respectively. The positions for the hydrogen atoms were calculated geometrically with one exception for O(14) (BuOH), which was found from the difference electron synthesis and refined using riding model. All structures was refined by a full-matrix least-squares against F^2 in the anisotropic-(H-isotropic) approximation. All calculations were carried out on an IBM PC with SHELXTL PLUS 5 (gamma-version) programs. Crystal data and details of the X-ray experiments are given in Table 1. The atomic coordinates and displacement parameters for structure **2** are listed in the Table 2.

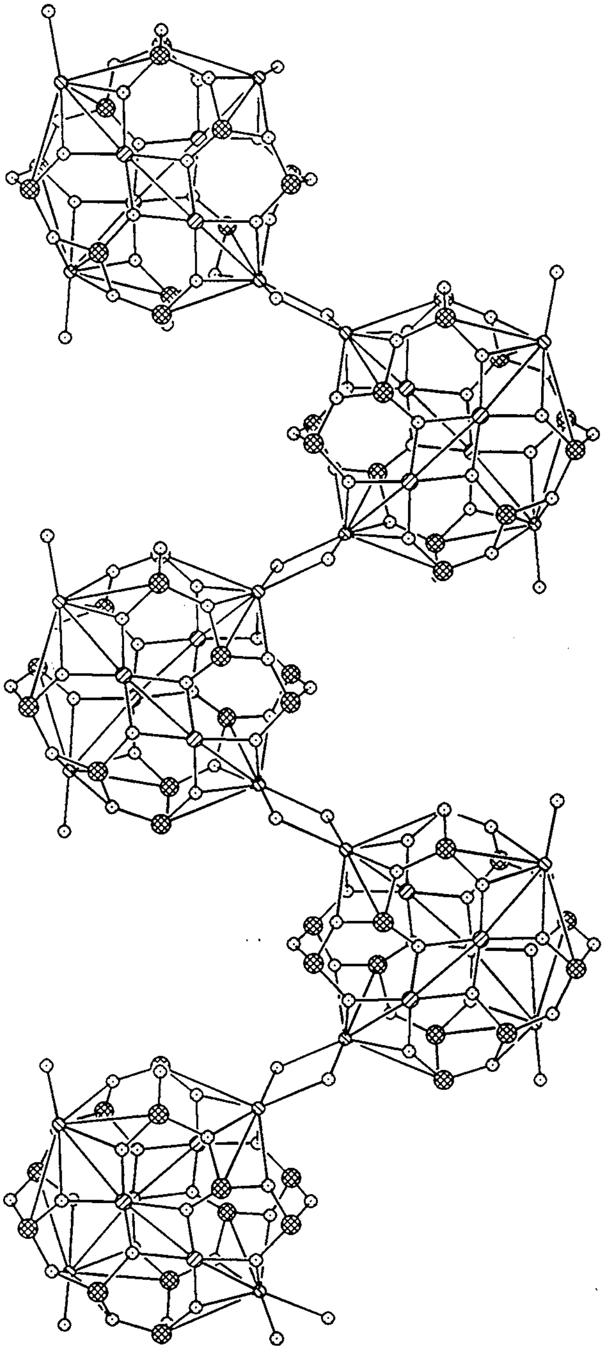


Fig. 2. The zig-zag chains in the crystal structure **2**. The Vi and Bu groups are omitted for clarity.

*3.2. Synthesis of copper/sodium-phenylsiloxane **1a** from PhSi(OBu)$_3$*

The mixture of *n*-butanol (45 ml), 4.38 g (13.50 mmol) of phenyltributoxysilane, water (0.24 g, 13.50 mmol) and 0.54 g (13.50 mmol) of sodium hydroxide was stirred and refluxed for 1 h. Then 0.61 g (4.50 mmol) of copper chloride (anhydrous) were dissolved in 6 ml *n*-butanol and this solution was added dropwise to the boiling reaction mixture through a drop funnel. After the addition of the $CuCl_2$ solution was completed the reaction mixture was refluxed for 15 min. The hot solution was filtered (to remove NaCl). The filtrate was evaporated in half on a rotor-vapor. Precipitated blue crystals were filtered and dried at reduced pressure (90°, 1 mm Hg). Yield of the crystals is 1 g (41.8%). Anal. Calc. (%): $\{Na_4[C_6H_5Si(O)O]_{12}(Cu)_4\}$ $(C_4H_9OH)\cdot(H_2O)$; C,42.43; H,3.42; Si, 15.84; Cu, 10.96; Na, 3.62; for $_{76}H_{72}Si_{12}Cu_4Na_4O_{26}$.. Anal. Found (%): C, 43.78; H, 3.48; Si, 16.17; Cu, 12.19; Na, 4.41.

*3.3. Synthesis of copper/sodium-phenylsiloxane, **1b** from PhSi(OMe)$_3$*

The mixture of $PhSi(OMe)_3$ (12.78 g, 64.44 mmol), NaOH (2.58 g, 64.44 mmol) and H_2O (1.16 ml, 64.44 mmol) in 120 ml of toluene was heated under reflux for 1 h until a transparent solution was obtained. After that the solution was refluxed for 30 min. To that solution $CuCl_2$ (2.89 g, 21.48 mmol) in 15 ml of methanol was added and the reaction mixture was vigorously stirred under reflux for 30 min. After filtration of the NaCl precipitate and partial evaporation of the solvent, blue crystals were formed, filtered and dried in vacuum (1 mm Hg) at 80–90°C. Yield is 5.8 g (42.2%) of product. Anal. Calc. (%): $\{Na_4[C_6H_5Si(O)O]_{12}(Cu)_4\}\cdot(CH_3OH)_3(H_2O)_6$. C, 41.0; H, 3.85; Si, 15.34; Cu, 11.57; Na, 4.19 for $C_{75}H_{84}Si_{12}Cu_4Na_4O_{33}$. Anal. Found (%): C, 40.17; H, 3.86; Si, 14.88; Cu, 11.92; Na, 4.10.

*3.4. Synthesis of copper/sodium-vinylsiloxanolate **2** from ViSi(OMe)$_3$*

ViSi(OMe)$_3$ (3.88 g, 26.17 mmol), NaOH (1.05 g, 26.17 mmol) were stirred for 2 h in 80 ml of 96% ethanol. To that a solution of CuCl$_2$ (1.17 g, 8.72 mmol) in 12 ml of ethanol was added and the resulting mixture was stirred at room temperature for another 1 h. After filtration of the NaCl precipitate 1 ml (55.51 mmol) water was added and the solution was heated to boil and allowed to cool to room temperature. It was then stored over night. The blue crystals formed were separated off and dried under vacuum (1 mm Hg/80°C). The mother liquor was concentrated and a second part of blue crystals was isolated. Yield is 2.5 g (75.5%) of the main product.

A suitable crystal for X-ray analysis was prepared after recrystallization from *n*-butanol. Anal. Calc. (%): $\{Na_4[C_2H_3Si(O)O]_{12}(Cu)_4\}(C_2H_5OH)_1(H_2O)_5$. C, 20.43; H, 3.43; Si, 22.06; Cu, 16.63; Na, 6.02 for $C_{26}H_{52}Si_{12}Cu_4Na_4O_{30}$. Anal. Found (%): C, 19.83; H, 3.06; Si, 21.99; Cu, 17.50; Na, 6.06.

*3.5. Trimethylsilylation of copper/sodium-phenylsiloxanolate **1a***

Crystals of copper/sodium-phenylsiloxane **1a** (1g, 0.48 mmol) were added to the mixture of Me$_3$SiCl (28.78 mmol, 3.13 g), pyridine (23.03 mmol, 1.82 g, 0.6 ml) and benzene (30 ml) under vigorous stirring at room temperature. The reaction mixture was refluxed for 20 min, cooled, filtered from precipitate, washed from HCl, evaporated from solvent and dried (1 mm Hg/80°C).The white solid product obtained was washed with ethanol. 0.74 g (61%) of $[PhSi(O)OSiMe_3]_{12}$ was obtained. Anal. Calc. (%): $[C_6H_5Si(O)OSi(CH_3)_3]_{12}$. C, 51.38; H, 6.71; Si, 26.70 for $C_{108}H_{168}Si_{24}O_{24}$.Anal. Found (%): C, 50.95; H, 6.59; Si, 26.31. ^{29}Si-NMR δ: 8.76 (s) ppm (*cis/cis*-OSiMe$_3$), 9.76 (s) ppm (*cis/trans*-OSiMe$_3$) and -80.67 (s) ppm (O$_3$SiPh). ^{1}H-NMR δ: two singlets at -0.107 ppm (*cis/cis*-SiMe$_3$) and -0.336 ppm (*cis/trans*-SiMe$_3$) with the ratio of integrated intensities 1:2. The ratio of integrated intensities of the phenyl region (6.5–7.5 ppm) to both the methyl signals comes to 5:9. GPC: RT = 16.04 (for standard RT = 16.01) ([6]a).

*3.6. Trimethylsilylation of copper/sodium-phenylsiloxanolate **1b***

An amount of 4.15 g (yield 63%) of white crystalline product was obtained from 5.8 g (2.64 mmol) of **1b** and 17.22 g (158.42 mmol) of Me$_3$SiCl in benzene (80 ml) in the presence of pyridine (10.02 g, 126.73 mmol) in much the same way as 3.5. Anal. Calc. (%): $[C_6H_5Si(O)OSi(CH_3)_3]_{12}$. C, 51.38; H, 6.71; Si, 26.70 for $C_{108}H_{168}Si_{24}O_{24}$. Anal. Found (%): C, 51.22; H, 6.28; Si, 26.47. ^{29}Si-NMR δ: 8.81 ppm (*cis/cis*-OSiMe$_3$), 9.80 ppm (*cis/trans*-OSiMe$_3$) and -80.69 ppm (O$_3$SiPh). ^{1}H-NMR δ: two singlets at -0.103 ppm (*cis/cis*-SiMe$_3$) and -0.330 ppm (*cis/trans*-SiMe$_3$) with the ratio of integrated intensities 1:2. The ratio of integrated intensities of phenyl region (6.5–7.5 ppm) to both methyl signals comes to 5:9. GPC: RT = 16.05 (for standard RT = 16.01 [6]a).

Acknowledgements

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References

[1] (a) O.I. Shchegolikhina, A.A. Zhdanov, V.A. Igonin, Yu.E. Ovchinnikov, V.E. Shklover, Yu. T. Struchkov, Organomet. Chem. USSR 4 (1991) 39. (b) V.A. Igonin, S.V, Lindeman, K.A. Potekhin, V.E. Shklover, Yu. T. Struchkov, O.I. Shchegolikhina, A.A. Zhdanov, I.V. Razumovskaya, Organomet. Chem. USSR 4 (1991) 383. (c) V.A, Igonin, S.V. Lindeman, Yu. T. Struchkov, O.I. Shchegolikhina, A.A. Zhdanov, Yu. A. Molodtsova, I.V. Razumovskaya, Organomet. Chem. USSR 4 (1991) 672. (d) V.A. Igonin, O.I. Shchegolikhina, S.V. Lindeman, M.M. Levitsky, Yu. T. Srtuchkov, A.A. Zhdanov, J. Organomet. Chem. 423 (1992) 351.

[2] (a) V.A. Igonin, S.V. Lindeman, Yu. T. Struchkov, O.I. Shchegolikhina, Yu. A. Molodtsova, Yu. A. Pozdniakova, A.A. Zhdanov, Russ. Chem. Bull. 42 (1993) 168. (b) V.A. Igonin, S.V. Lindeman, Yu. T. Struchkov, Yu. A. Molodtsova, Yu. A. Pozdniakova, O.I. Shchegolikhina, A.A. Zhdanov, Russ. Chem. Bull. 42 (1993) 176.

[3] A.A. Zhdanov, O.I. Shchegolikhina, Yu. A. Molodtsova, Russ. Chem. Bull. 42 (1993) 917.

[4] M.G. Voronkov, S.V. Basenko, Heterolytic cleavage reactions of the siloxane bond, Sov. Sci. Rev. B 15 (1990) 1.

[5] (a) K.A. Andrianov, A.I. Chernyshev, V.A. Temnikovskii, V.V. Yastrebov, V.M. Kopylov, Teoret. I Eksp. Khimya 11 (1975) 5. (b) V.M. Kopylov, A.I. Chernyshev, P.L. Prihod'ko, in: 1st USSR Conference on Chemistry and Application of Organosilicon Compounds (Tbilisi, 1980), Abstracts of Papers, pt.II, NITEKhIM, Moscow, 1980, pp.482 (in Russian). (c) K.A. Andrianov, A.I. Chernyshev, V.M. Kopylov, P.L. Prihod'ko, S.E. Esipov, Zh. Obshch. Khimii 50 (1980) 5 1044.

[6] (a) O.I. Shchegolikhina, I.V. Blagodatskikh, A.A. Zhdanov, Cage–like oligo(phenylmetallasiloxane)s', in: Robert Corriu, Peter Jutzi, Braunschweig (Eds.), Tailor-Made Silicon-Oxygen Compounds. From Molecules to Matrials', Wiesbaden, Vieweg, 1996, pp. 177. (b) I.V. Blagodatskikh, O.I. Shchegolikhina, Yu. A. Pozdnyakova, Yu. A. Molodtsova, A.A. Zhdanov., Russian Chem. Bull. 43 (1994) 993.

[7] R. Shannon, Acta Crystallogr. Sect. A 32 (1976) 75.

[8] V.E. Shklover, Yu.T. Struchkov, in: M.G. Voronkov, (Ed.), Advances in Organosilicon Chemistry, Mir, Moscow, 1985, pp. 11–36.