

# Copper/sodium-directed hydrolytic condensation of methyltriethoxysilane: Self-assembly of polyhedral Cu/Na-methylsiloxane. Synthesis and properties of new stereoregular macrocyclosiloxane

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## Abstract

A hydrolytic condensation of methyltriethoxysilane was performed in the presence of sodium and copper ions. A crystalline copper/sodium-methylsiloxane of a general formula  $\{\text{Na}_4[(\text{MeSi}(\text{O})\text{O})_{12}\text{Cu}_4]\} \cdot 6(n\text{-BuOH})$  (**1a**) was obtained as the only product in a high yield. X-ray analysis of a single crystal obtained after recrystallization of **1a** by slow diffusion of methanol vapours into its ethanol solution was characterised as  $\{\text{Na}_4[(\text{MeSi}(\text{O})\text{O})_{12}\text{Cu}_4]\} \cdot 4(\text{MeOH}) \cdot 4(\text{EtOH})$  (**1b**). In the crystal molecules are assembled into zig-zag chains by O–H···O bonds. Removal of metal ions by a reaction of **1a** or **1b** with  $\text{Me}_3\text{SiCl}$  gave a new siloxane macrocycle tris-*cis*-tris-*trans*-dodecamethyldodecatrimethylsiloxycyclododecasiloxane,  $[\text{MeSi}(\text{O})\text{OSiMe}_3]_{12}$  (**2**), in a high yield.

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## 1. Introduction

The hydrolytic condensation of trifunctional organosilanes (e.g.  $\text{RSiCl}_3$  or  $\text{RSi}(\text{OR}')_3$ ), which are generally used for the preparation of silsesquioxane materials, is a multistep and complicated process [1]. A statistical distribution of intermediate components generated in the reaction media makes the process extremely sensitive to changes in experimental conditions and usually produces a wide range of products. The aim of our investigations is to direct the hydrolytic condensation of trifunctional

silanes to the formation of only one desired compound with well-defined structure, using a template. The template is designed to assemble silicon-containing species through non-covalent bonding, bringing functional groups attached at silicon atoms into close proximity. This favors cyclocondensation and, finally, the formation of well-organized architectures. Subsequent removal of the template gives an individual cyclosiloxane molecule with a well-defined structure.

As an alternative to the traditional approaches used in siloxane chemistry we have taken advantage of metal ion-directed self-assembly strategy to selectively create cage-like metallasiloxane molecules with well-defined architectures by hydrolytic condensation of various

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trifunctional alkoxy silanes in the presence of alkaline and transition or lanthanide metal ions [2]. The metal ions were used both as templating entities and as structural elements.

Metallasiloxanes are very interesting and promising compounds as models of catalytic systems [3] and as precursors of molecular magnets [4]. Besides they are a unique source of new stereoregular siloxane cycles many of which cannot be synthesized by the traditional reactions of siloxane chemistry. A reaction of metallasiloxanes with triorganylchlorosilanes or dilute hydrochloric acid allowed us to remove metal ions as metal chlorides and obtain siloxane cycles [2a,2c,5,6]. These cycles contain two different types of “covering” on both sides of a cycle plane – essentially distinguished on character of intermolecular interactions. Due to this the cycles obtained exhibit interesting physical properties. Many of them are mesomorphic compounds [5b,5c].

Continuing our work on the metal-directed hydrolytic condensation of trialkoxy silanes resulting in self-assembly of metallasiloxanes and creation of new stereoregular siloxane cycles we present here the synthesis, molecular and crystalline structure of a new Cu/Na-containing methylsiloxane as well as the synthesis and characterization of a siloxane macrocycle derived from it.

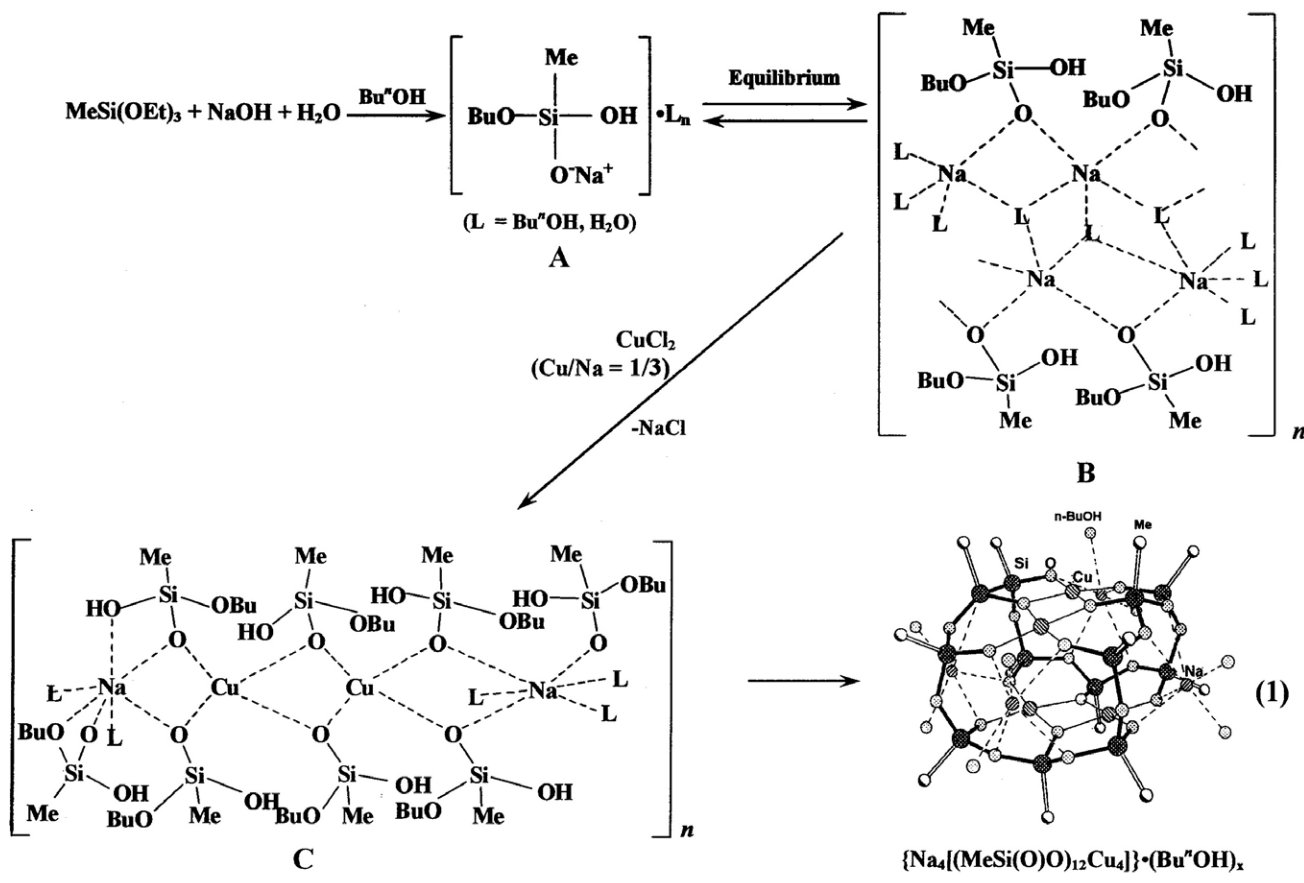
## 2. Results and discussion

### 2.1. Synthesis of Cu/Na-containing methylsiloxane (1) and tris-cis-tris-trans-dodecamethyl-dodecatrimethylsiloxycyclododecasiloxane (2)

The synthesis of a new crystalline Cu/Na-containing methylsiloxane was carried out in two steps according to Scheme 1.

The first step involved the hydrolysis of  $\text{MeSi}(\text{OEt})_3$  in the presence of equimolar amount of  $\text{NaOH}$  in *n*-butanol generating in situ a labile alkaline intermediate **A** [6] containing ion pairs. This tends to associate (Equilibrium I) [7] forming complex aggregates **B** in which ionic components (alkali metal ions, alcohol and water molecules) are surrounded by silicon species containing functional OH and OR groups. After the addition of solution of  $\text{CuCl}_2$  partial exchange of sodium ions by bivalent Cu (II) ions takes place as shown on the second step, resulting in a formation of aggregates **C**. Under reaction conditions the functional groups attached to organosilicon fragments are involved in condensation to form organosiloxanolate rings on a “metallic matrix,” *i.e.*, Cu/Na-methylsiloxane molecule (1).

After the complete removal of the solvent from the resulting solution the compound **1a** was isolated as a blue



Scheme 1. Scheme of the synthesis of Cu/Na-methylsiloxane 1.

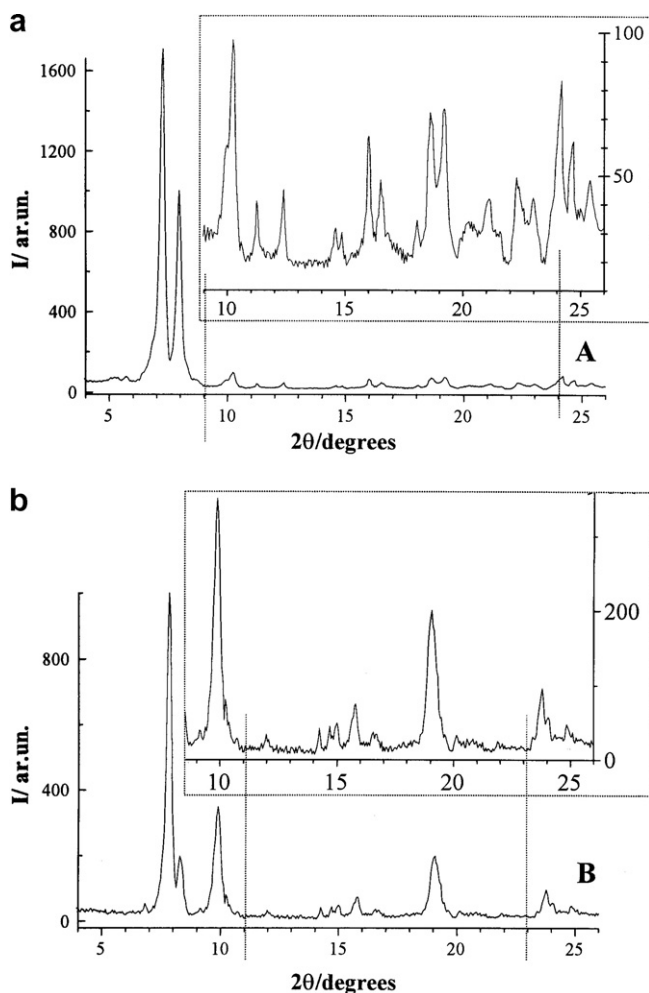
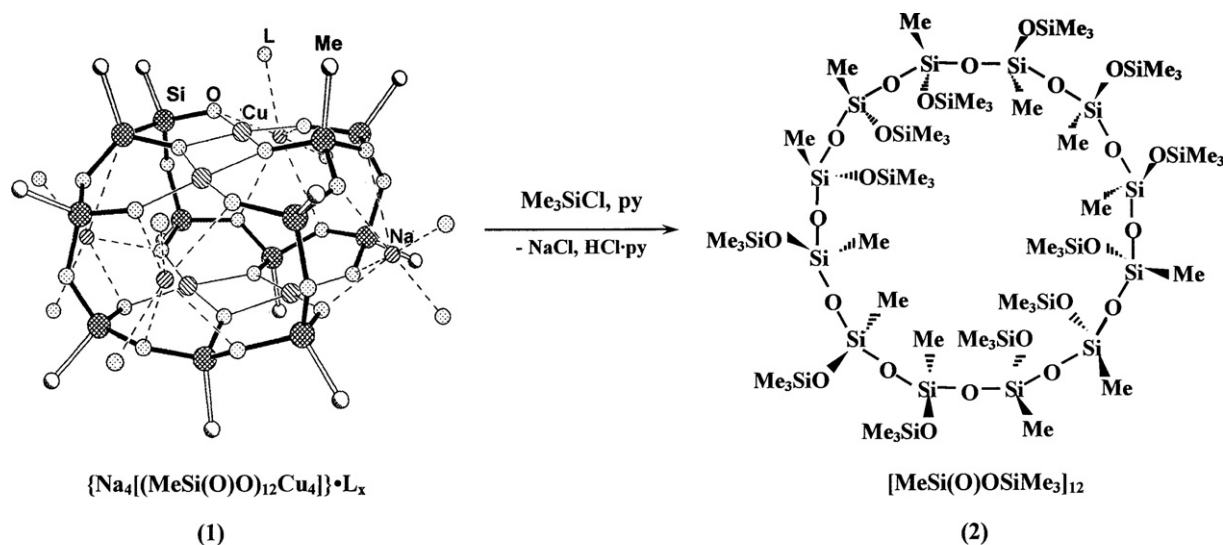


Figure 1. XRD patterns of **1a** and **1b** obtained at 20 °C.



**1a:** L = n-BuOH;

**1b:** L = MeOH, EtOH.

solid with a yield up to 76.5%. XRD study of the product showed that it was a crystalline substance (Fig. 1, curves A, a). A recrystallization of **1a** by slow diffusion of methanol vapours into its ethanol solution gave blue crystals **1b** in a few days. A powder diffractogram characterizing the whole bulk of crystalline product **1b** is shown in Fig. 1 (curves B, b). XRD study of the products **1a** and **1b** (Fig. 1) showed that they were completely crystalline. The crystallite sizes for **1a** and **1b** were comparable.

The treatment of **1a** and **1b** with  $Me_3SiCl$  (Scheme 2) gave viscous clear colourless liquids with good yields in both cases. In accordance to elemental analyses, NMR spectra and HPSEC data these two trimethylsiloxy-derivatives were identical substances and corresponded to the formula of tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-dodecamethyldodecatrimethylsilyloxycyclododecasiloxane,  $[MeSi(O)OSiMe_3]_{12}$  (compound **2**). Thus, this suggests that the metallasiloxane core of products **1a** and **1b** was the same.

X-ray diffraction study of a single crystal isolated from the crystalline mass of **1b** was identified to be  $\{Na_4[(MeSi(O)O)_{12}Cu_4]\} \cdot 4(MeOH) \cdot 4(EtOH)$  (Fig. 2); details of the study are discussed below (see Section 2.2).

Based on the single crystal X-ray diffraction study of **1b**, results of trimethylsilylation of **1a** and **1b** and the elemental analysis of **1a** (see Section 4.3) we concluded that the molecular formula for **1a** can be represented as  $\{Na_4[(MeSi(O)O)_{12}Cu_4]\} \cdot 6(n-BuOH)$ . The difference between molecular formulas of **1a** and **1b** is limited to the type of solvents in the crystal. Complex **1a** was obtained by evaporation of the mother liquor as a solid and **1b** was isolated as crystals from ethanol solution. However, both complexes have the same metallasiloxane core.

Scheme 2. Scheme of the synthesis of **2**.

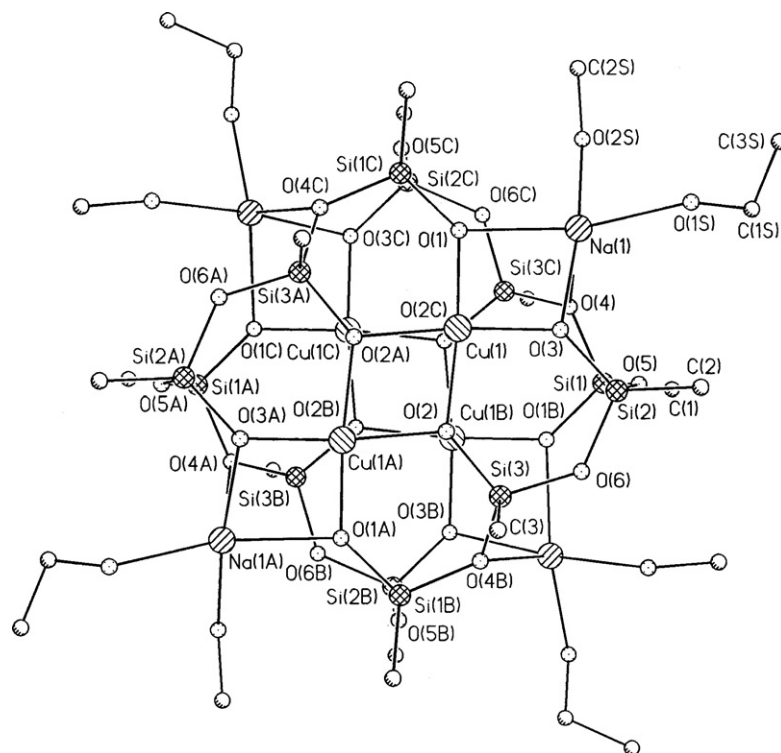


Figure 2. The general view and numbering scheme of the complexes **1a** (Me and Et groups are omitted for clarity).

## 2.2. Crystal structure of **1b**

The basic experimental X-ray details and crystal parameters are given in Table 1. The molecular structure of **1b** with the atomic numbering scheme is presented in Fig. 2 and selected bond lengths and bond angles are given in Table 2.

Table 1  
Crystal data and details of the X-ray experiments for **1a**.

Empirical formula	C <sub>24</sub> H <sub>76</sub> Cu <sub>4</sub> Na <sub>4</sub> O <sub>32</sub> Si <sub>12</sub>
Formula weight	1560.05
Crystal colour, habit	Blue prism
Temperature (K)	193(2)
Crystal system	Tetragonal
Space group	<i>P</i> <sub>4</sub> <sub>2</sub> / <i>n</i>
<i>a</i> (Å)	15.025(3)
<i>c</i> (Å)	13.467(3)
<i>V</i> (Å <sup>3</sup> )	3040.2(11)
<i>Z</i> ( <i>Z'</i> )	2(0.25)
<i>F</i> (000)	1608
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.704
Linear absorption, $\mu$ (cm <sup>-1</sup> )	17.28
Scan type	$\theta/2\theta$
2 $\theta$ max (°)	55
Completeness of dataset (%)	98.0
Reflections measured	4589
Independent reflections [ <i>R</i> <sub>int</sub> ]	3453 [0.0643]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1966
Parameters	176
Final <i>R</i> ( <i>F</i> <sub>hk</sub> ): <i>R</i> <sub>1</sub>	0.0497
<i>wR</i> <sub>2</sub>	0.1192
Goodness-of-fit	1.017
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.354, -0.262

The molecule **1b** in crystal occupies the special 4-fold inversion axis position passing through the middle of the

Table 2  
Selected bond lengths (Å) and angles (°) for **1a**

Bond lengths			
Cu(1)–O(1)	1.915(3)	Si(3)–O(6)	1.628(3)
Cu(1)–O(3)	1.934(3)	Si(3)–O(4)**	1.638(3)
Cu(1)–O(2)	1.945(3)	Na(1)–O(2S)	2.307(5)
Cu(1)–O(2)*	1.954(3)	Na(1)–O(1)	2.336(4)
Si(1)–O(1)**	1.588(3)	Na(1)–O(3)	2.347(4)
Si(1)–O(5)	1.625(3)	Na(1)–O(1S)	2.352(4)
Si(1)–O(4)	1.661(3)	Na(1)–O(4)	2.734(4)
Si(2)–O(3)	1.597(3)	O(1)–Si(1)***	1.588(3)
Si(2)–O(5)	1.637(3)	O(2)–Cu(1)*	1.954(3)
Si(2)–O(6)	1.654(3)	O(4)–Si(3)***	1.637(3)
Si(3)–O(2)	1.604(3)		
Bond angles			
O(1)–Cu(1)–O(3)	92.5(1)	O(2)–Si(3)–O(6)	109.4(2)
O(1)–Cu(1)–O(2)	168.8(2)	O(2)–Si(3)–O(4)**	109.0(2)
O(3)–Cu(1)–O(2)	94.4(1)	O(6)–Si(3)–O(4)**	106.5(2)
O(1)–Cu(1)–O(2)*	96.2(1)	Si(1)***–O(1)–Cu(1)	134.7(2)
O(3)–Cu(1)–O(2)*	166.0(1)	Si(1)***–O(1)–Na(1)	129.4(2)
O(2)–Cu(1)–O(2)*	78.8(2)	Si(3)–O(2)–Cu(1)	133.8(2)
O(1)**–Si(1)–O(5)	113.5(2)	Si(3)–O(2)–Cu(1)*	124.8(2)
O(1)**–Si(1)–O(4)	110.4(2)	Cu(1)–O(2)–Cu(1)*	100.8(2)
O(5)–Si(1)–O(4)	104.4(2)	Si(2)–O(3)–Cu(1)	130.3(2)
O(3)–Si(2)–O(5)	111.4(2)	Si(3)***–O(4)–Si(1)	123.7(2)
O(3)–Si(2)–O(6)	111.2(2)	Si(1)–O(5)–Si(2)	139.5(2)
O(5)–Si(2)–O(6)	105.8(2)	Si(3)–O(6)–Si(2)	130.4(2)

Atoms labelled by \*, \*\*, \*\*\* are generated from the reference atoms by the:

$-x + 1/2$ ,  $-y + 1/2$ ,  $z$ ;  $-y + 1/2$ ,  $-z + 1/2$  and  $y$ ,  $-x + 1/2$ ,  $-z + 1/2$  symmetry transformations, respectively.

Cu···Cu lines (Fig. 2). The bond lengths and angles as well as conformation of siloxanolate ring and manner of its coordination with copper atoms in **1b** are similar to the corresponding ones in the  $\{\text{Na}_4[(\text{PhSi}(\text{O})\text{O})_{12}\text{Cu}_4]\} \cdot 8(n\text{-BuOH})$  (**3**) and  $\{\text{Na}_4[(\text{CH}_2=\text{CHSi}(\text{O})\text{O})_{12}\text{Cu}_4]\} \cdot 4(n\text{-BuOH})$  (**4**) complexes [2a,8].

In the molecule **1b** the cyclododecasiloxanolate ligand is characterised by tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*) configuration. In further discussion oxygen atoms of the siloxanolate ligand bounded to the metal atoms will be indicated as  $\text{O}_m$ , whereas others belonging to the cycle ligand will be written as  $\text{O}_c$ . The Cu atoms in **1b** are characterised by significantly distorted square planar coordination with decrease of the O(1)Cu(1)O(2) and O(3)Cu(1)O(2A) angles to  $168.8(2)^\circ$  and  $166.0(1)^\circ$ . The Cu– $\text{O}_m$  distances vary in the narrow range (1.915(3)–1.953(3) Å) with Cu– $\text{O}_m$  (bridging) being the longest. The angles at the bridging  $\text{O}_m$  atoms ( $100.8(2)^\circ$ ) are similar to the corresponding values in **3** and **4** ( $101.7(3)^\circ$  and  $101.3(3)^\circ$ , respectively). The  $\text{Cu}_2\text{O}_6$  moieties have “staggered” orientation (the Cu atoms are projected to  $\text{O}_m$ ). It is noteworthy that  $\text{Cu}_2\text{O}_6$  moiety is characterised by a significant twist with the dihedral angle between Cu(1)O(2)O(2A)Cu(1A) and O(1)Cu(1)O(3) planes equal to  $16^\circ$ . In spite of the aforementioned distortions of the copper coordination in **1b** the Cu(1)···Cu(1A) separations in **1b**, **3** and **4** (3.001(1), 3.06 and 3.008(2) Å, correspondingly) are equal to each other. The distance between the dimeric moieties  $\text{Cu}_2\text{O}_6$  in **1b** is largest (3.912(3) Å) in this row of copper/sodium-organosiloxanes (3.386(3) Å for **3** and 3.371(3) Å for **4**). In all cases (**1b**, **3** and **4**) the apical coordination of Cu atom by  $\text{O}_m$  atom of the neighbouring  $\text{Cu}_2\text{O}_6$  unit is excluded.

The  $\text{O}_m\text{--Si--O}_m$  and  $\text{Si--O}_c\text{--Si}$  bond angles are typical for this class of compounds values (Table 2).

Six-membered siloxanolate copper containing cycles in the molecule of **1b** are characterized by two different conformations. The Cu(1)O(2)O(3)Si(2)O(6)Si(3) cycle-like analogous cycles in **3** and **4**, have the boat conformation with deviation of the Si(3) and O(3) atoms by 0.28 and 0.37 Å, respectively, while the Si(1)O(4)O(1A)Si(3A)Cu(1-B)O(2B) have the half-chair conformation with deviation of the Si(3A) atom (0.62 Å).

Sodium ions in the structure **1b** are five-coordinated; their coordination spheres are composed from two solvent

molecules and only three oxygens of cyclododecasiloxanolate ligand (two  $\text{O}_m$  and one  $\text{O}_c$ ). This differs from complexes **3** and **4** where the coordination sphere of sodium ions included four oxygen atoms (two  $\text{O}_m$  and two  $\text{O}_c$ ). Moreover the Na– $\text{O}_c$  distance in **1b** is significantly elongated (2.736(4) Å) in comparison with Na– $\text{O}_m$  (2.308(5)–2.351(5) Å). Probably, this asymmetry of sodium coordination leads to the distortions of the metallasiloxanolate cycles and as the result of the copper tetrahedron.

The self-assembly of metallasiloxanes in the crystal (Fig. 3) is accomplished by two different types of interaction: ionic alkali metal···O bonds or by hydrogen bonds formed by the solvate molecules.

The molecules in **1b** are assembled into zig-zag chains only by O–H···O hydrogen bonds of moderate strength between the hydrogen atoms of solvent molecules and  $\text{O}_m$  oxygens (O(1S)–H(1S)···O(3') ( $1-x$ ,  $1-y$ ,  $-z$ ) H(1S)···O(3') 2.10 Å, O(1S)···O(3') 2.805(3) Å; O(1S)–H(1S)O(3')  $167^\circ$ ) (see Fig. 3).

### 2.3. Characterization of **2**

Tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-configuration of the molecule **2** was established by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra. At first the investigation was carried out in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR spectrum has two single non-equivalent signals of Me-groups attached to silicon atoms of siloxane cycle and to siloxy-groups with the ratio of integrated intensities 1:3, respectively (Fig. 4a). Each of  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra has pair of non-equivalent signals splitted into two peaks of *cis/cis*- and *cis/trans*-arrangement of atom groups (Figs. 5 and 6).

When the toluene- $d_8$  was used as a solvent to investigate the dynamics of the ring motion it was found that  $^1\text{H}$  NMR spectrum has two non-equivalent signals splitted into two peaks corresponding to *cis/cis*- and *cis/trans*-arrangement of atom groups (Fig. 4b). The study carried out in a temperature range from 23 to  $80^\circ\text{C}$  demonstrated an absence of any changes of  $^1\text{H}$  NMR spectrum (neither chemical shifts nor width of peaks).

The molecular mass of **2** was established by electrospray mass spectrometry. The nominal ion mass of **2** at 1796.3 amu was assigned to the ammoniated adduct of  $[\text{MeSi}(\text{O})\text{OSiMe}_3]_{12}$  (formula weight, 1778).

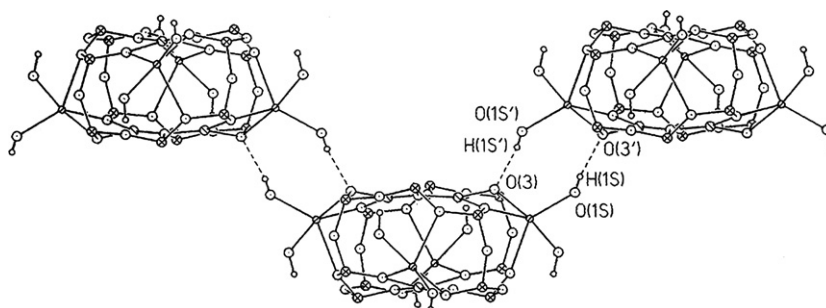


Figure 3. The zig-zag chain in the crystal structure **1a** (Me and Et groups are omitted for clarity).

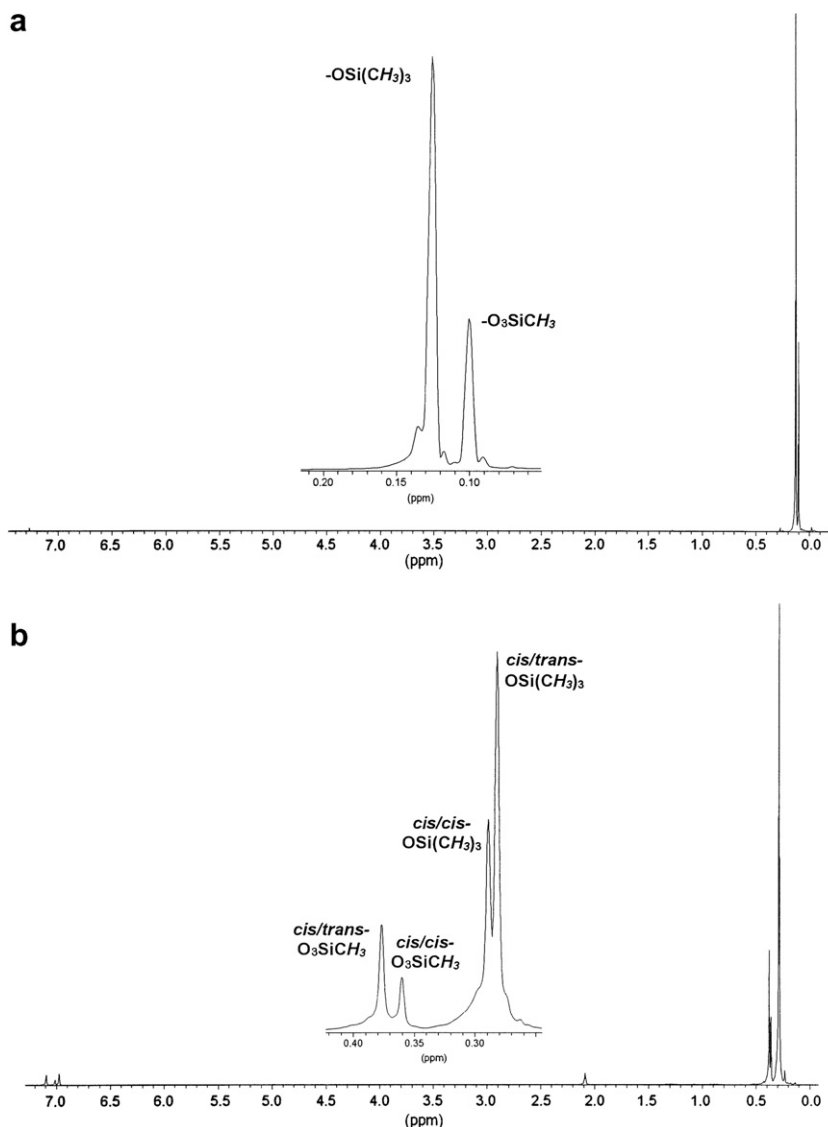


Figure 4.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$  solution (a), in toluene- $d_8$  solution (b).

Compound **2** is a viscous clear colourless liquid at room temperature ( $n_D^{20} = 1.4130$ ) which is stable up to  $200^\circ\text{C}$  according to TGA and DTA data (Fig. 7).

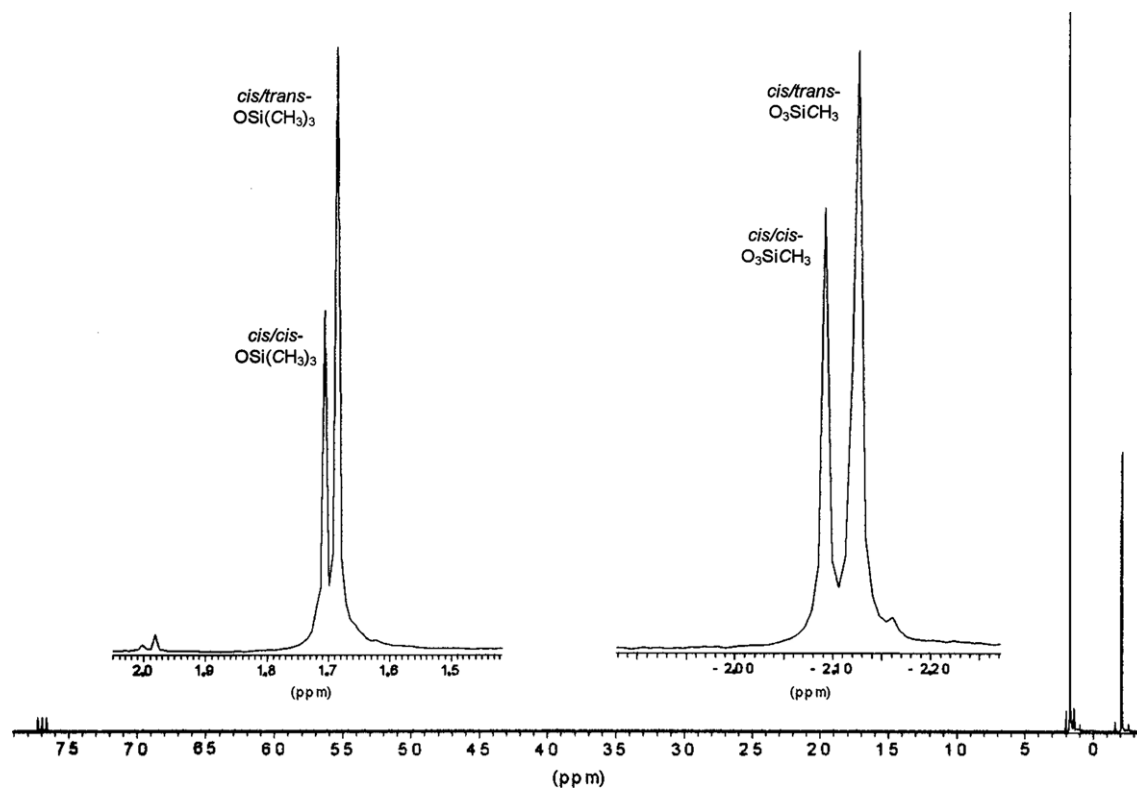
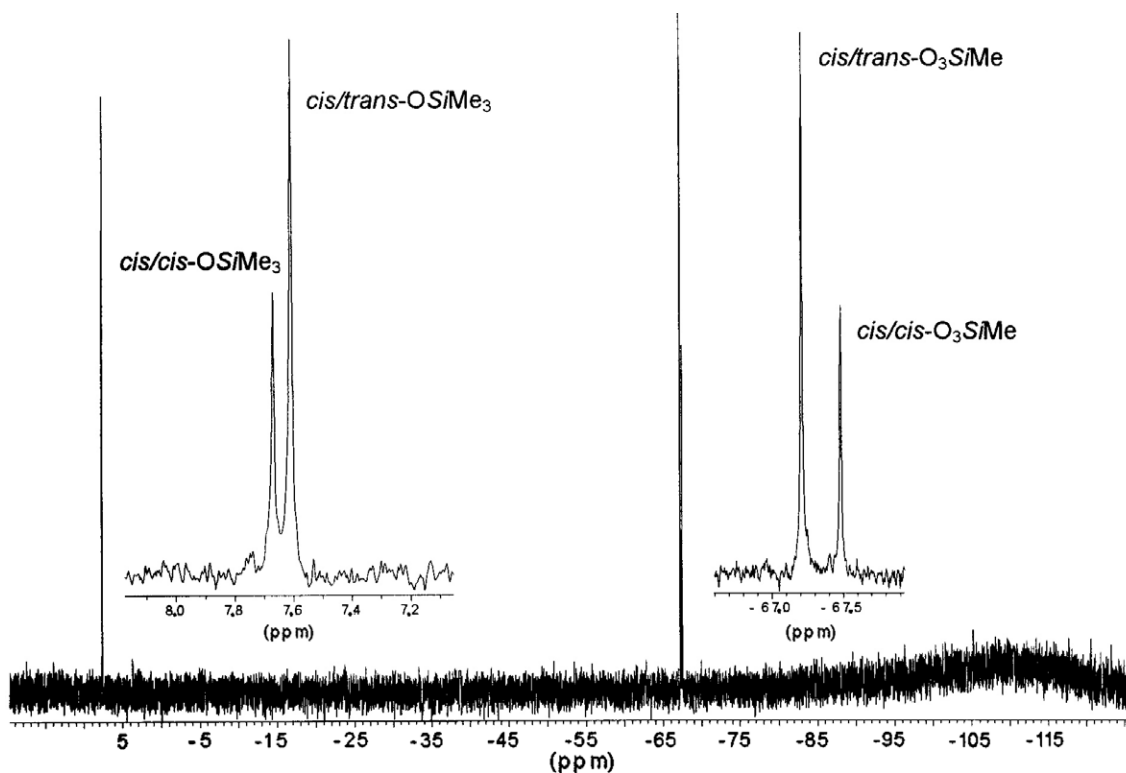
The DSC measurements did not detect any crystallization at low temperatures, only a glass transition was found at  $-93^\circ\text{C}$  (Fig. 8).

The X-ray diffraction pattern of **2** is not typical for a liquid organosiloxane. As a rule, XRD patterns of liquid cyclic and linear organosiloxanes comprise of two halos [9]: the first one is located in the angular region of  $2\theta^* = 4\text{--}14^\circ$  and the second one – in the region of  $2\theta^{**} = 15\text{--}40^\circ$ . As example three typical diffractograms for liquid siloxanes – deca-*k*is-trimethylsilyloxytetrasiloxane  $\text{Me}_3\text{SiO}[\text{SiO}(\text{OSiMe}_3)_2]_4\text{OSiMe}_3$  (DTMS) (curve 1), octamethylcyclotetrasiloxane (OMCTS) (curve 2), and oligodimethylsiloxane (ODMS,  $n = 10$ ) (curve 3) – are presented in Fig. 9.

In general, the character of the intensity distribution for the amorphous scattering in the area of  $2\theta^*$  determines the

statistics of average intermolecular distances, while the intensity distribution curve in the second angular region  $2\theta^{**}$  is mainly determined by the average intramolecular distances. Experimentally this peculiarity of the scattering of siloxanes appears as a shift of the  $2\theta^*$  value towards the region of smaller angles as the size of the siloxane molecule increases. This tendency is visually demonstrated in Fig. 9 (curves 1, 2 and 3): in the row ODM-S  $\rightarrow$  OMCTS  $\rightarrow$  DTMS one can see the  $2\theta^*$  value shifted to smaller angle region as the average intermolecular distances increase due to the chemical structure of the siloxanes. Distinctively different from these three organosiloxanes, **2** shows quite complex diffraction pattern (Fig. 9, curve 4). Indeed, one can see several overlapping amorphous halos in the first angular region  $2\theta^*$ , where the first one at a maximum at  $2\theta_1^* = 7.02^\circ$  is distinguished by a relatively small half-width,  $\Delta_{1/2} \approx 1.5^\circ$ .

To explain the uncommon XRD-pattern for **2**, we compared it with the X-ray data obtained for another

Figure 5.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$  solution.Figure 6.  $^{29}\text{Si}$  NMR spectrum of **2** in  $\text{CDCl}_3$  solution.

24-membered cycle in the liquid-like state, that is tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-[ $\text{CH}_2=\text{CHSi}(\text{O})\text{-OSiMe}_3$ ] $_{12}$  (**5**) [2a] (Fig. 9, curves 4 and 5). The comparison

has shown that the XRD-patterns of **2** and **5** are very similar. These cyclosiloxanes comprise of two types of side groups where  $\text{R}' = \text{Me}$  for **2** and  $\text{CH}_2=\text{CH}$  for **5** and

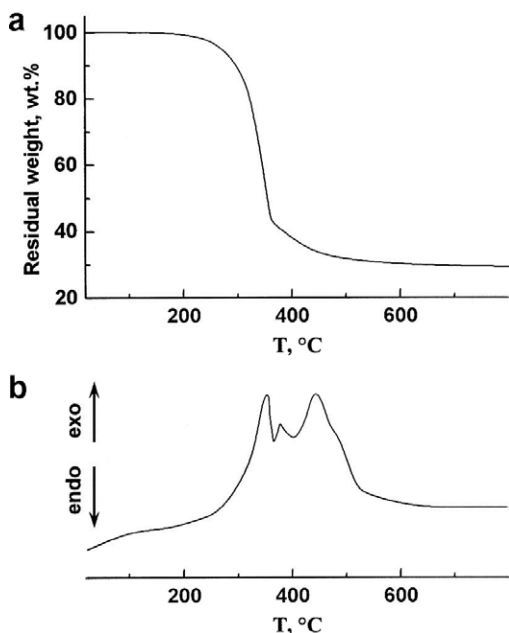


Figure 7. TG (a) and DTA (b) curves for **2**; sample in air, heating rate 5 deg/min.

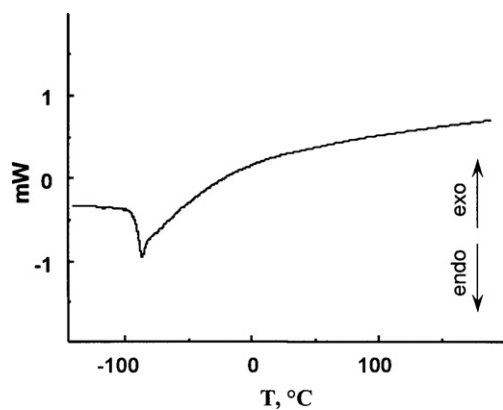


Figure 8. DSC curve obtained for **2**, heating rate 10 deg/min.

$R'' - \text{OSiMe}_3$  for **2** and **5**. The size of the side groups  $R''$  for both **2** and **5** are identical, while the size of the side groups  $R'$  are different. In the XRD-patterns in Fig. 6 it is seen that the  $2\theta_1^*$  values for these compounds differ slightly, whereas the angular position of the second halo  $2\theta_1^*$  for **5** is shifted towards smaller angular regions as the size of the side groups  $R'$  increases. Hence, the appearance of the two well-defined halos in the first angular region at  $2\theta^* = 4\text{--}14^\circ$  should be attributed to the presence of predominantly two types of inter- and intra-molecular contacts, i.e.  $\text{Si-R}'\cdots\text{R}'\text{-Si}$  and  $\text{Si-R}''\cdots\text{R}''\text{-Si}$ . We believe that the unique structure and high flexibility of liquid 24-membered organocyclosiloxanes cause the microphase separation on inter- and intramolecular levels. As a result, molecules of these compounds can form substructures in a liquid state. The investigation of these compounds is in a progress now and the results will be published separately.

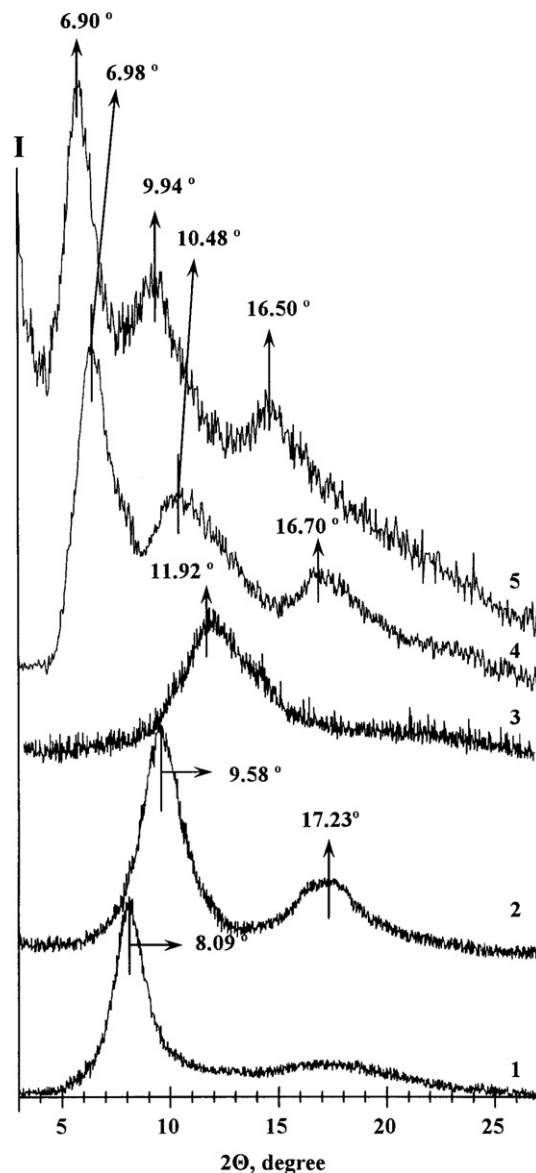


Figure 9. XRD patterns of DTMS (curve 1), OMCTS (curve 2), ODMS (curve 3), **2** (curve 4) and **5** (curve 5), obtained at 20 °C.

The rheological behavior of **2** suggests that it behaves as Newtonian liquid. The flow curves obtained for **2** at various temperatures demonstrate an independence of viscosity values from shear rate in the temperature range of 20–165 °C (Fig. 10a). The energy of viscous flow obtained from the flow curves is 26 kJ/mol that is approximately twice of the value for PDMS (Fig. 10b).

### 3. Conclusion

New crystalline polyhedral Cu/Na-containing methylsiloxane **1** was obtained in a good yield by a hydrolytic condensation of methyltriethoxysilane directed by sodium and copper(II) ions, and well characterized. Compound **1** is a unique source for the synthesis of a new 24-membered stereoregular organosiloxane macrocycle **2** with methyl and



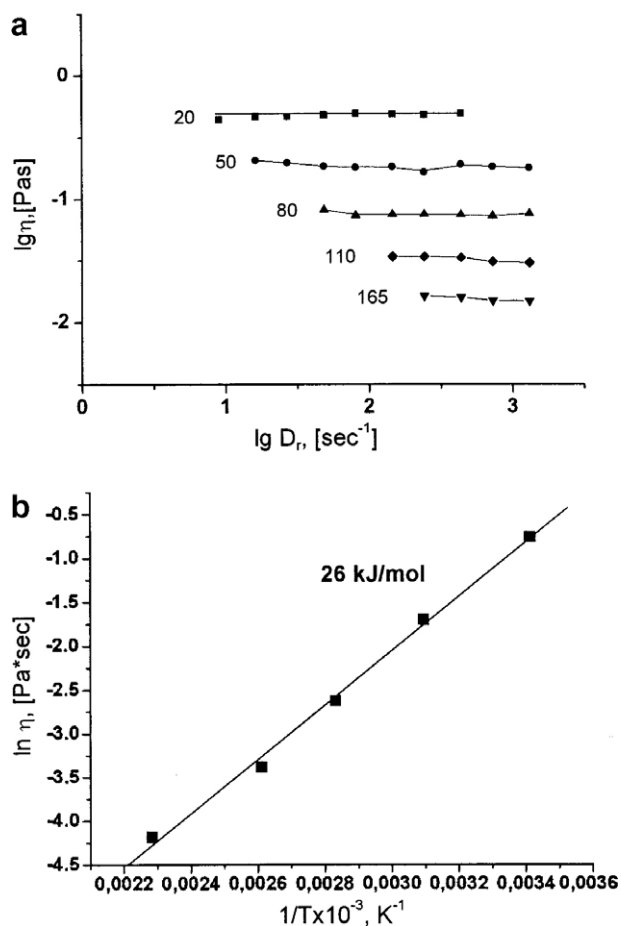


Figure 10. Temperature dependence of viscous flow (a) and energy of viscous flow (b) for **2**.

trimethylsiloxy substituents at silicon atoms. The compound is a viscous liquid that can be characterized as a Newtonian liquid due to an independence of viscosity values from shear rate in a wide temperature region.

## 4. Materials and methods

### 4.1. Materials

Methyltriethoxysilane, trimethylchlorosilane, pyridine, 1-butanol, ethanol, methanol and hexane were purchased from Aldrich; NaOH of analytical grade was used. Anhydrous CuCl<sub>2</sub> was prepared by heating its crystal hydrate at 120 °C to a constant weight.

### 4.2. Methods

X-ray characterization was performed with filtered Cu K $\alpha$  radiation using DRON-3M X-ray diffractometer with an asymmetric focusing monochromator (a bent quartz crystal). <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded with a Bruker WP-SY200 spectrometer (200.13 MHz for <sup>1</sup>H, 39.76 MHz for <sup>29</sup>Si) at 20 °C in CDCl<sub>3</sub> solution and in a

temperature range 23–80 °C in toluene-*d*<sub>8</sub> solution with TMS as an internal reference standard.

The HPSEC was carried out on U-Styragel 1000 and 500 Å columns using Waters Instrument with IR-detector M410 and Maxima software. Toluene was used as eluent, flow rate was 1 ml/min. [PhSi(O)OSiMe<sub>3</sub>]<sub>12</sub> (retention time is RT = 18.78 min) and [PhSi(O)OSiMe<sub>3</sub>]<sub>6</sub> (RT = 19.50 min) well-characterized previously [5a] were used as standards. The coinciding of TMS-substituted phenyl- and methylcyclosiloxanes peak positions suggests that the molecular volumes of these TMS-derivatives are similar.

The ESI-MS spectrum for **2** was recorded on a PE Sciex triple quadrupole API 350 mass spectrometer, using positive ion mode in MeOH/CHCl<sub>3</sub> mixture that contained NH<sub>4</sub>COOCH<sub>3</sub> as a source of NH<sub>4</sub><sup>+</sup> for ion adduct formation with the siloxane compound.

The density of **2** was measured using a pycnometer at 20 °C.

The refraction index of **2** was measured using a refractometer IRF-22 (USSR) at 20 °C.

X-ray in single crystal diffraction study: details of crystal data, data collection and structure refinement parameters for the structure of **1b** are given in Tables 1 and 2. The structure was solved by direct method and refined by the full-matrix least-squares technique against *F*<sup>2</sup> with the anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located from the Fourier difference electron density synthesis and included in refinement in the isotropic approximation. All calculations were performed using SHELXTL-97 [10] on IBM PC AT.

DSC measurements were carried out on a 6 mg sample under argon on Mettler-Toledo-822e using a standard technique with heating rate 10 deg/min. The thermal stability was established by TGA measurements on the Derivatograph-C (MOM, Hungary) in air at heating rates of 5 deg/min using about 20 mg sample.

### 4.3. Synthesis of **1a**

A three-neck flask was charged with 40 mL of *n*-BuOH, 1.00 g (0.025 mol) of NaOH and 1.36 g (0.075 mol) of water. After dissolution of NaOH a solution of 4.47 g MeSi(OEt)<sub>3</sub> (0.025 mol) in 10 mL of *n*-BuOH was added dropwise under vigorous stirring at room temperature. Then 3.62 g (0.2 mol) of water was added dropwise. The reaction mixture was heated to reflux and a solution of CuCl<sub>2</sub> (1.12 g, 0.0084 mol) in 30 mL of *n*-BuOH was added dropwise. The reaction mass was refluxed for 5 min, and then filtered through two-folded paper filter. The resulted deep-blue colored solution was evaporated from the solvent on the rotor-vapor and dried in vacuum (1 mm Hg/80 °C). An amount of 2.7 g (76.5 %) of bright-blue crystalline product was obtained. Anal. Calc. for {Na<sub>4</sub>[(MeSi(O)O)<sub>12</sub>Cu<sub>4</sub>]} · 6(*n*-BuOH), C<sub>36</sub>H<sub>96</sub>Si<sub>12</sub>Cu<sub>4</sub>Na<sub>4</sub>O<sub>30</sub>: C, 25.54; H, 5.72; Si, 19.91; Cu, 15.02; Na, 5.44. Found: C, 24.48; H, 5.12; Si, 19.32; Cu, 14.50; Na, 6.11%.

#### 4.4. Preparation of **1b**

An amount of 0.9 g of **1a** was dissolved in hot ethanol and the resulted solution was stored in a desiccator in the presence of methanol. An amount of 0.85 g (94.4 %) of bright-blue needle-like crystals **1b** were isolated and dried in vacuum (1 mm Hg/ 80 °C). Anal. Calc. for  $\{\text{Na}_4[(\text{MeSi}(\text{O})\text{O})_{12}\text{Cu}_4]\} \cdot (\text{EtOH}) \cdot 3(\text{H}_2\text{O})$ ,  $\text{C}_{14}\text{H}_{48}\text{Si}_{12}\text{Cu}_4\text{Na}_4\text{O}_{28}$ : C, 12.48; H, 3.59; Si, 25.01; Cu, 18.86; Na, 6.83. Found: C, 12.47; H, 3.52; Si, 24.00; Cu, 17.80; Na, 6.76%.

#### 4.5. Synthesis of **2** from **1a**

Compound **1a** (0.9 g, 0.53 mmol) and pyridine (2.52 g, 31.91 mmol) were mixed in a three-necked flask and stirred for 10 min at the room temperature. A solution of trimethylchlorosilane (4.16 g, 38.29 mmol) in 25 mL of hexane was added dropwise under vigorous stirring. The reaction mixture was stirred for another 20 min at room temperature and then was refluxed for 1 h. The resulting mixture was cooled to room temperature, washed with water to remove  $\text{Cl}^-$ , dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. After drying in vacuum (1 mm Hg/ 50 °C, 1 h), 0.78 g (82.1%) of viscous colorless product was obtained. Anal. Calc. for  $[\text{MeSi}(\text{O})\text{OSiMe}_3]_{12}$ ,  $\text{C}_{48}\text{H}_{144}\text{Si}_{24}\text{O}_{24}$ : C, 32.39; H, 8.16; Si, 37.88. Found: C, 32.50; H, 7.95; Si, 37.80%.  $^1\text{H}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  0.12 (9H, s,  $-\text{OSi}(\text{CH}_3)_3$ ) and 0.10 (3H, s,  $-\text{O}_3\text{SiCH}_3$ ) with the ratio of integrated intensities 3:1.  $^1\text{H}$  NMR (MHz, toluene- $d_8$ , TMS), ppm:  $\delta$  0.38 (3H, *cis/trans*- $\text{O}_3\text{SiCH}_3$ ) and 0.36 (3H, *cis/cis*- $\text{O}_3\text{SiCH}_3$ ) with the ratio of integrated intensities 2:1, 0.29 (9H, *cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ) and 0.28 (9H, *cis/trans*- $\text{OSi}(\text{CH}_3)_3$ ) with the ratio of integrated intensities 1:2.  $^{13}\text{C}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  1.69 (3C, s, *cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ), 1.67 (3C, s, *cis/trans*- $\text{OSi}(\text{CH}_3)_3$ ),  $-2.11$  (1C, s, *cis/cis*- $\text{O}_3\text{SiCH}_3$ ),  $-2.14$  (1C, s, *cis/trans*- $\text{O}_3\text{SiCH}_3$ ).  $^{29}\text{Si}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  7.67 (*cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ), 7.61 (*cis/trans*- $\text{OSi}(\text{CH}_3)_3$ ),  $-67.21$  (*cis/trans*- $\text{O}_3\text{SiCH}_3$ ),  $-67.48$  (*cis/cis*- $\text{O}_3\text{SiCH}_3$ ); RT = 18.79 min;  $n_D^{20} = 1.4130$ ;  $d_4^{20} = 0.9926$  g/ml.

#### 4.6. Synthesis of **2** from **1b**

Analogously to the synthesis described above, 0.85 g (76.5 %) of **2** were obtained from 0.85 g (0.63 mmol) of **1b** and 5.2 g (47.92 mmol) of  $\text{Me}_3\text{SiCl}$  in 20 mL of hexane in the presence of 3.19 g (40.35 mmol) of pyridine. Anal. Calc. for  $[\text{MeSi}(\text{O})\text{OSiMe}_3]_{12}$ ,  $\text{C}_{48}\text{H}_{144}\text{Si}_{24}\text{O}_{24}$ : C, 32.39; H, 8.16; Si, 37.88. Found: C, 32.55; H, 8.36; Si, 37.72%.  $^1\text{H}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  0.12 (9H, s,  $-\text{OSi}(\text{CH}_3)_3$ ) and 0.10 (3H, s,  $-\text{O}_3\text{SiCH}_3$ ) with the ratio of integrated intensities 3:1.  $^1\text{H}$  NMR (MHz, toluene- $d_8$ , TMS), ppm:  $\delta$  0.38 (3H, *cis/trans*- $\text{O}_3\text{SiCH}_3$ ) and 0.36 (3H, *cis/cis*- $\text{O}_3\text{SiCH}_3$ ) with the ratio of integrated intensities 2:1, 0.29 (9H, *cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ) and 0.28 (9H, *cis/*

*trans*- $\text{OSi}(\text{CH}_3)_3$ ) with the ratio of integrated intensities 1:2.  $^{13}\text{C}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  1.69 (3C, s, *cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ), 1.67 (3C, s, *cis/trans*- $\text{OSi}(\text{CH}_3)_3$ ),  $-2.11$  (1C, s, *cis/cis*- $\text{O}_3\text{SiCH}_3$ ),  $-2.14$  (1C, s, *cis/trans*- $\text{O}_3\text{SiCH}_3$ ).  $^{29}\text{Si}$  NMR (MHz,  $\text{CDCl}_3$ , TMS), ppm:  $\delta$  7.67 (*cis/cis*- $\text{OSi}(\text{CH}_3)_3$ ), 7.61 (*cis/trans*- $\text{OSi}(\text{CH}_3)_3$ ),  $-67.21$  (*cis/trans*- $\text{O}_3\text{SiCH}_3$ ),  $-67.48$  (*cis/cis*- $\text{O}_3\text{SiCH}_3$ ); RT = 18.78 min;  $n_D^{20} = 1.4130$ ;  $d_4^{20} = 0.9930$  g/ml.

#### Acknowledgement

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#### Appendix A. Supplementary material

CCDC 659661 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.002](https://doi.org/10.1016/j.jorganchem.2008.02.002).

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