Reactions of cage-like copper/sodium organosiloxanes with $CuCl_2$

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The reactions of cage-like copper/sodium organosiloxanes with $CuCl_2$ were studied. Cage-like copper organosiloxanes containing the Si—O—Cu—Cl group were synthesized for the first time.

Key words: cage-like copper/sodium organosiloxanes, copper(II) chloride, cage-like copper organosiloxanes, X-ray diffraction analysis.

Earlier,[1—3] we have synthesized cage-like copper/sodium(potassium) organosiloxanes with phenyl, vinyl, ethyl, or methyl substituents at the silicon atom and established their structures. The first step of the synthesis involved the preparation of sodium or potassium organosilanolate based on organosilsesquioxanes or organotrialkoxysilanes

$$[RSiO_{1.5}]_n + 0.5n\ MOH + 0.5n\ M \longrightarrow [RSi(O)OM]_n,$$

$$n RSi(OR')_3 + n MOH + n H_2O \longrightarrow [RSi(O)OM]_n + 3n R'OH,$$

followed by metathesis with copper chloride

$$12[RSi(O)OM]_n + 4n\ CuCl_2 \longrightarrow n[RSiO_{1.5}]_{12}[CuO]_4[MO_{0.5}]_4 + 8n\ MCl.$$

X-ray diffraction study of the structures of copper organosiloxanes demonstrated that all these compounds, except for copper/potassium ethylsiloxane, have structures of the same type based on the saddle-like 12-membered siloxane ring fixed by four copper atoms and four sodium atoms. Copper/potassium ethylsiloxane has a sandwich structure based on two six-membered siloxane rings linked by four copper atoms and two potassium atoms. Two other potassium atoms are located in the outer sphere of the molecule, one of them being coordinated to the lower siloxane ring of the cage and another one being coordinated to the upper siloxane ring.

† Deceased.

In a series of cage-like copper organosiloxanes devoid of alkali metal atoms, only copper phenylsiloxane $[PhSiO_{1.5}]_6[CuO]_6[PhSiO_{1.5}]_6$ having a sandwich structure has been described.[4] The aim of the present study was to synthesize new copper organosiloxanes, in particular, copper vinyl- and methylsiloxanes devoid of alkali metals.

Results and Discussion

Attempts to use a standard synthesis procedure in alcoholic solutions (methanol, ethanol, butanol, or their combinations) for the preparation of copper vinyl- and methylsiloxanes failed.

The synthesis of known copper-containing phenylsiloxane (**1**) with the use of a 1,4-dioxane—alcoholic mixture (instead of an alcoholic solution) made it possible to increase the yield of this compound to 64%. However, this mixture appeared to be inefficient in the synthesis of the corresponding vinyl and methyl derivatives. Hence, we attempted to perform the stepwise replacement of the sodium atoms, *i.e.*, we initially synthesized known copper/sodium vinyl- and methylsiloxanes **2a** and **2b**, respectively, and then we intended to replace the remaining sodium atoms according to the equation

$$[RSiO_{1.5}]_{12}[CuO]_4[NaO_{0.5}]_4 + 2\ CuCl_2 \xrightarrow[\textbf{2a,b}]{} [RSiO_{1.5}]_{12}[CuO]_6 + 4\ NaCl,$$

R = CH_2=CH, Me.

We found that copper chloride does not react with copper/sodium vinylsiloxane **2a** in pure dioxane, whereas

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the addition of small amounts of alcohol gives rise to an insoluble precipitate. The reaction in a dioxane—DMSO mixture afforded a small amount of blue crystals. Analysis demonstrated that these crystals contained chlorine; the Si : Cu : Cl ratio was 12 : 8 : 4. Unlike the known cage-like metallasiloxanes, this compound is insoluble in dioxane, butanol, ethyl acetate, and an ethanol—toluene mixture. After recrystallization of this compound from dioxane—DMSO or toluene—DMSO mixtures, the Si : Cu : Cl ratio remained unchanged. We considered $[CH_2{=}CHSiO_{1.5}]_{12}[CuO]_4[CuO_{0.5}Cl]_4$ (**3a**) as a probable formula of this product. A change in the ratio between the starting reagents in accordance with this formula led to an increase in the yield of the crystalline compound from 30 to 73%.

The structure of this compound was established by X-ray diffraction analysis, which demonstrated that it has the formula $\mathbf{3a}\cdot 4Me_2SO\cdot 3C_7H_8$ (**3a´**) (Fig. 1) and contains eight copper atoms per cyclododecasiloxane ligand (L_{12}).

Compound **3a´** is the first structurally characterized copper complex with the L_{12} ligand devoid of alkali metal atoms, which is, apparently, responsible for the unusual features of its geometric structure.

The conformation, principal bond lengths, and bond angles in the cyclododecasiloxane ligand are virtually identical to the corresponding parameters of the copper vinylsiloxane complexes with the ratio Cu : L_{12} = 4 : 1 studied earlier.[1,5] In molecule **3a´**, the ligand adopts a tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*) con-

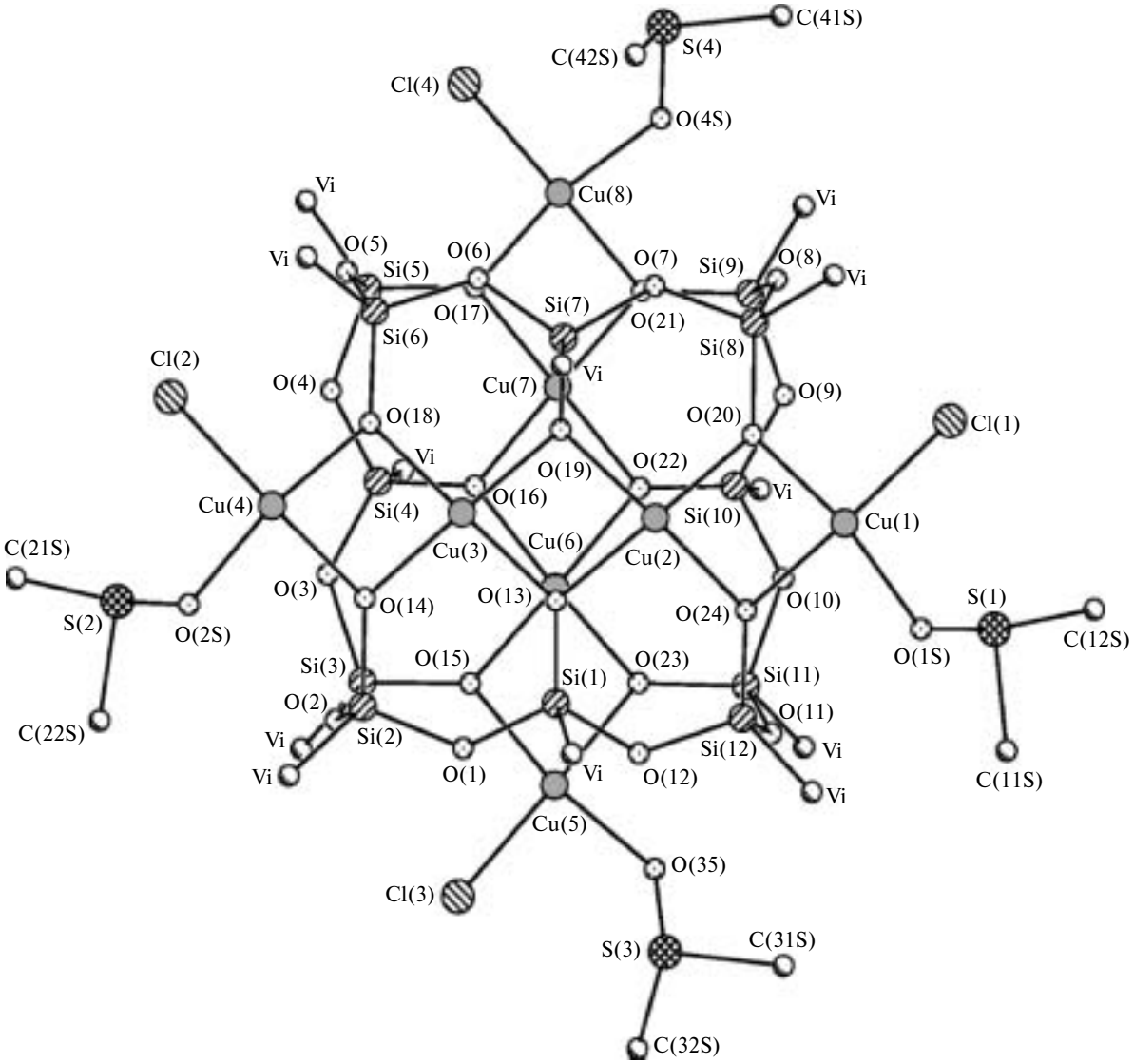

Fig. 1. Overall view of molecule **3a´**. The second positions of the disordered siloxanolate oxygen atoms and the copper atoms are omitted; Vi is vinyl.

figuration and a boat conformation. The O—Si—O bond angles (106.5(5)—115.7(4)°) are close to the ideal tetrahedral angle. The Si—O—Si bond angles (127.5(3)—139.1(2)°) are in the range typical of cyclic siloxanes.[6] The Si—O bond lengths are in the range of 1.600(5)—1.655(4) Å. All 12 siloxanolate oxygen atoms (O_M) in molecule **3a´**, unlike those in the complexes studied earlier, serve as μ_3-chelate bridges.

The coordination polyhedra of the copper atoms in complex **3a´** differ radically from those in the complexes involving the L_{12} ligand studied earlier. The differences are associated not only with the composition of the coordination sphere but also with the type of the coordination polyhedra of the copper atoms.

The copper atoms in complex **3a´** can be divided into two types, *viz.*, terminal (Cu(1), Cu(4), Cu(5), and Cu(8)) and central (Cu(2), Cu(3), Cu(7), and Cu(6)) atoms. The central copper atoms are coordinated only by the olate oxygen atoms of the ligand, whereas the coordination sphere of the terminal copper atoms involves also the chlorine atom and the DMSO molecule (see Fig. 1).

The coordination mode of the terminal copper atoms differs from that of the central copper atoms. The terminal copper atoms have a square-planar coordination (r.m.s. deviations of the atoms are in the range of 0.007—0.057 Å). By contrast, the coordination mode of the central copper atoms is ambiguous.

Analysis of difference Fourier maps and anisotropic displacement parameters demonstrated that the Cu(2), Cu(3), Cu(7), and Cu(6) atoms as well as the O_M atoms bound to these copper atoms are disordered over two positions with occupancies of 0.6 and 0.4. Two sets of copper atoms differ in the distance between the opposite Cu_2O_4 fragments. Hence, the disorder observed in complex **3a´** is presumably associated with the occurrence of intramolecular Cu...O interactions.

Since two Cu_4 fragments, like those in the complexes studied earlier, are arranged in a cross-like fashion, one would expect that a decrease in rigidity of the metallasiloxane cage will allow an additional apical Cu...O coordination between the opposite Cu_2O_4 fragments. Analysis of the corresponding distances showed that the distances between the Cu_2O_4 planes in molecule **3a´** for the copper atoms with an occupancy of 0.6 (Cu(2), Cu(3), Cu(6), and Cu(7)) is as short as 2.65 Å and the corresponding Cu...O distances are in the range of 2.59—2.73 Å. This range of distances indicates that the Cu(2), Cu(3), Cu(6), and Cu(7) atoms have a coordination number of 4 + 1 and the coordination involves the oxygen atom of the opposite Cu_2O_4 fragment located in the axial position of the tetragonal pyramid (Fig. 2, *a*).

By contrast, the analogous distance for the copper atoms with an occupancy of 0.4 (Cu(2A), Cu(3A), Cu(6A), and Cu(7A)) is as large as 3.92 Å. This distance is close to the corresponding values in the copper complexes with the L_{12} ligand studied earlier and completely excludes the intramolecular apical coordination of the Cu atoms by the O_M atoms.[1,5] Therefore, the Cu(2A), Cu(3A), Cu(6A), and Cu(7A) atoms, like the terminal copper atoms, are characterized by a square-planar coordination (Fig. 2, *b*).

A comparison of the geometry of the four- and five-coordinate copper atoms in molecule **3a´** demonstrates that the main differences are those in the Cu...Cu distances in the Cu_4 fragment. For the four-coordinate copper atoms, these distances are in the range of 2.848(2)—2.932(3) Å, whereas these distances in the chain containing the five-coordinate copper atoms are, on the average, longer (2.903(3)—2.933(2) Å), which may be indicative of the difference in their magnetic characteristics, for example, of the occurrence of superexchange through the oxygen bridges.

Consequently, the disorder observed in molecule **3a´** corresponds to a superposition of the complexes with and without the apical Cu...O_M interaction. This is evidence for a substantial decrease in rigidity of the metallasiloxane cage, which opens up possibilities for the use of the complexes with the ratio Cu : L_{12} = 8 : 1 for creating magnetically active materials.

Analysis of the crystal packing of **3a´** revealed the secondary Cl...S interactions, through which the molecules are linked in layers parallel to the crystallographic *bc* plane (Fig. 3). The shortened S...O distances (3.555(5)—3.608(5) Å) as well as the directionality of the interactions (Cl...S=O bond angles are ≈174°) suggest that these nonvalent contacts correspond to charge transfer from the lone electron pair of the chlorine atom to the antibonding orbital of the S—O group.

The toluene molecules of solvation are not involved in shortened contacts and are located both between the metallasiloxane layers and in the channels (diameter is ≈12.7 Å) extended parallel to the crystallographic *a* axis.

It is known[7] that treatment of cage-like organometallasiloxanes with trimethylchlorosilane in the presence of pyridine leads to the cleavage of the Si—O—M bond to form trimethylsilyl-substituted derivatives of the general formula $[RSiO(OSiMe_3)]_n$. Upon this treatment, the size and stereoregularity of the siloxane rings, which are the building blocks of the cage-like compound, are retained. This method combined with exclusion chromatography was used for studying uncrystallizable polymeric metallasiloxanes.[8]

Treatment of copper/sodium vinylsiloxane **2a** and copper chlorovinylsiloxane **3a** gave rise to the same vinylcyclosiloxane $[CH_2=CHSiO(OSiMe_3)]_{12}$ (**4a**). This fact was confirmed by ^1H NMR spectroscopy and gel-permeation chromatography.

The reaction of copper/sodium methylsiloxane **2b** with $CuCl_2$, like the reaction of compound **2a**, afforded crys-

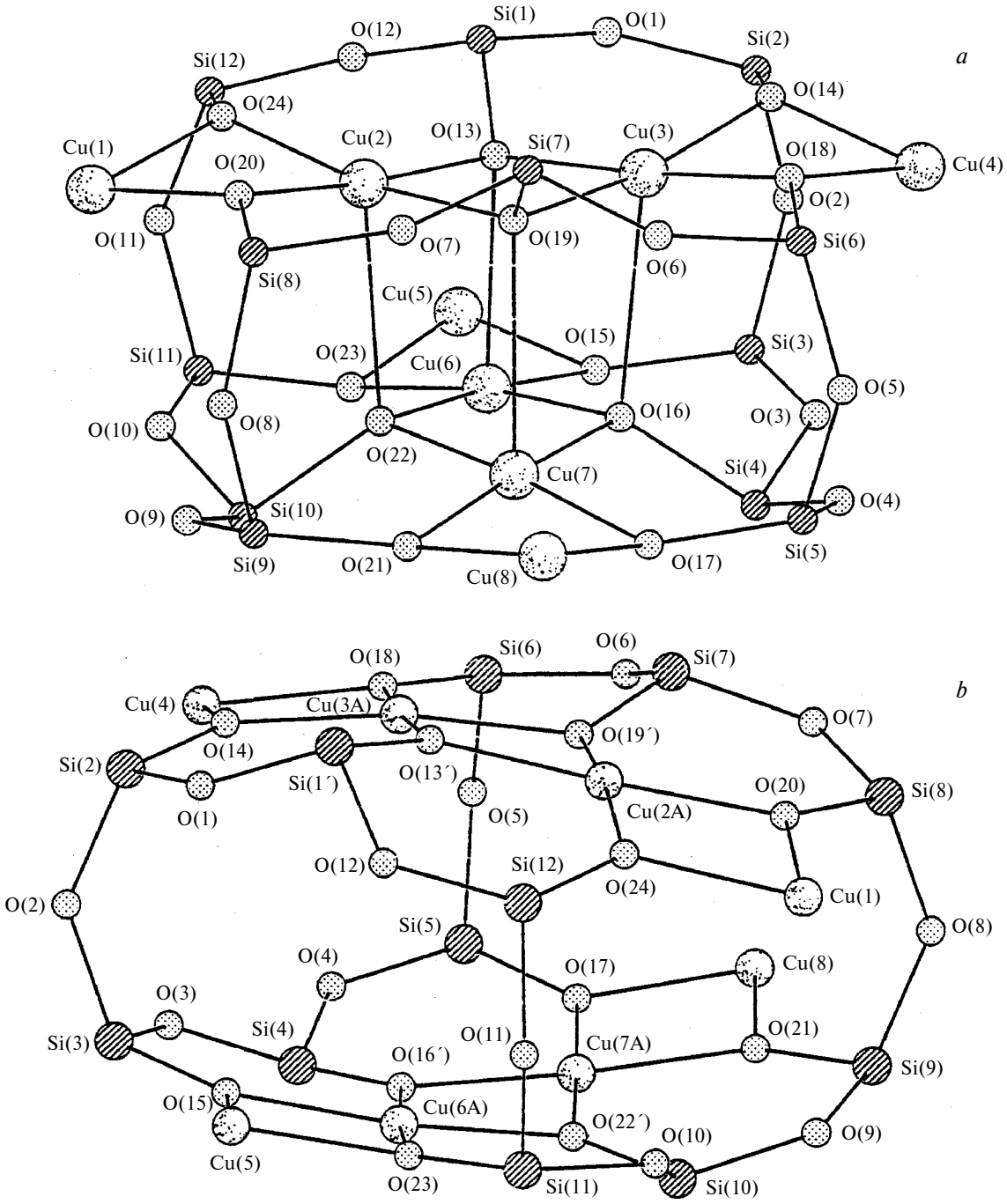

Fig. 2. Scheme illustrating the coordination mode of the central copper atoms in molecule **3a** for the positions with an occupancy of 0.6 (*a*) and the positions with an occupancy of 0.4 (*b*). The vinyl groups, the chlorine atoms, and the DMSO molecules are omitted.

talline compound **3b** with the ratio Si : Cu : Cl = 12 : 8 : 4 in 64% yield. We failed to grow crystals suitable for X-ray diffraction study. A comparison of the ^{29}Si NMR spectra and the elution volumes (Fig. 4) demonstrated that trimethylsilylation of compounds **2b** and **3b** produced the same methylcyclosiloxane $[MeSiO(OSiMe_3)]_{12}$ (**4b**). Elemental analysis data for compound **3b** and the results of NMR spectroscopy and GPC for its trimethylsilylation products suggest that the structure of **3b** is analogous to that of compound **3a´**, *i.e.*, it is based on the twelve-membered siloxane ring with four central copper atoms and four terminal CuCl groups.

To summarize, we demonstrated that the reactions of copper/sodium vinyl- and methylsiloxanes with $CuCl_2$ give rise to new copper complexes with the L_{12} ligand containing the Si—O—Cu—Cl groups.

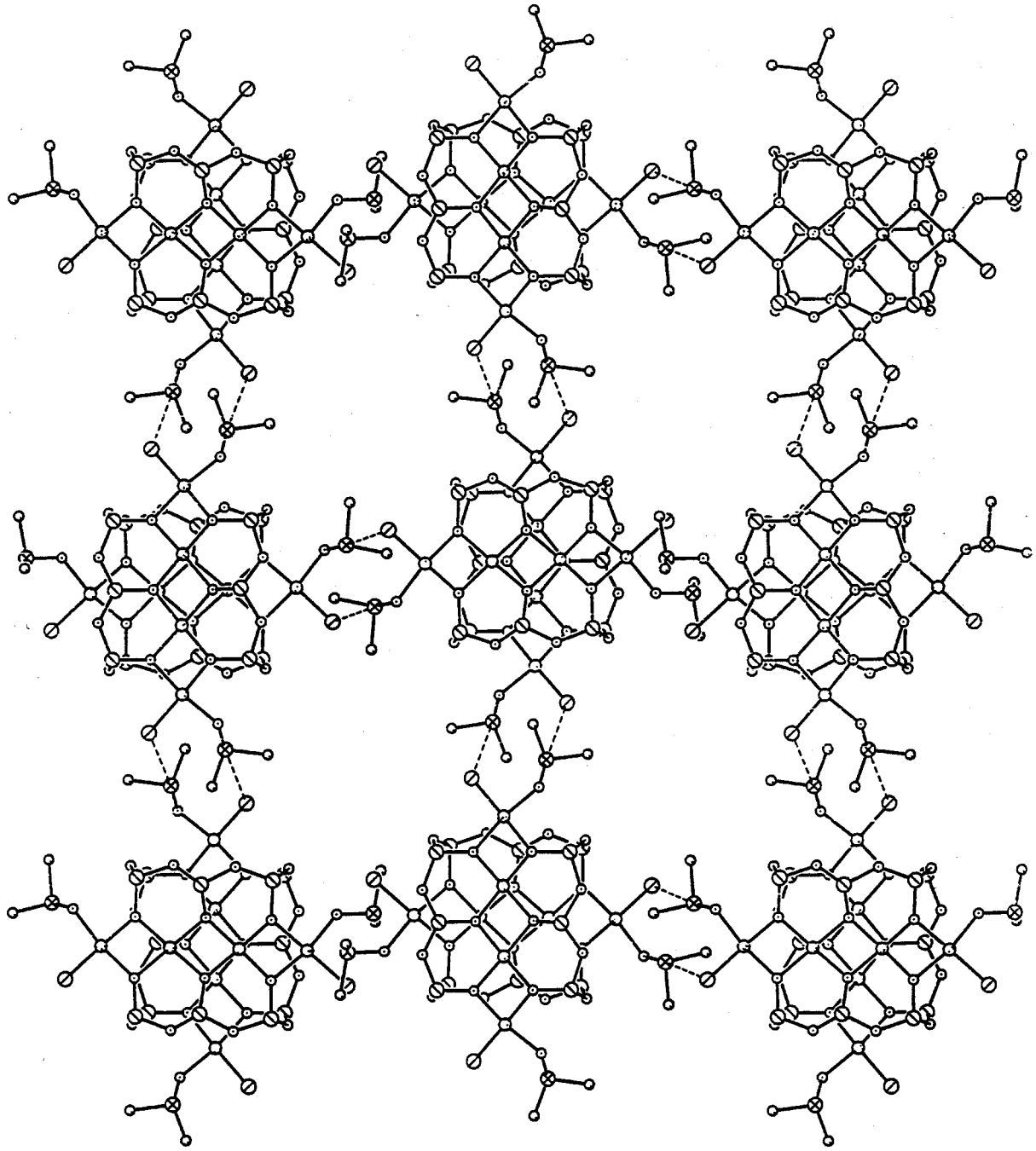

Fig. 3. Scheme illustrating the formation of layers in the structure of **3a´**. The vinyl substituents and the toluene molecules of solvation are omitted.

Experimental

The starting copper/sodium vinyl- and methylsiloxanes **2a** and **2b** were synthesized according to a known procedure.[3]

The ^1H and ^{29}Si NMR spectra were recorded on a Bruker WP-200SY spectrometer (200 MHz) in CCl_4.

Gel-permeation chromatograms were recorded on a Waters-510 instrument equipped with a refractometer detector and Ultrastyragel columns (10^2, 10^3, and 10^4 Å); THF was used as the eluent (flow rate was 1 mL min^{-1}; the temperature was 35 °C).

The molecular weights M_z were determined by sedimentation equilibrium on a 3180 analytical ultracentrifuge (MOM, Hungary); the rotor speed was 50000 rpm^{-1}; the temperature was 25 °C.

The low Si, Cu, and Cl contents and the high C and H contents in the metallasiloxanes are attributable to the presence of variable amounts of solvating solvents in the compounds.

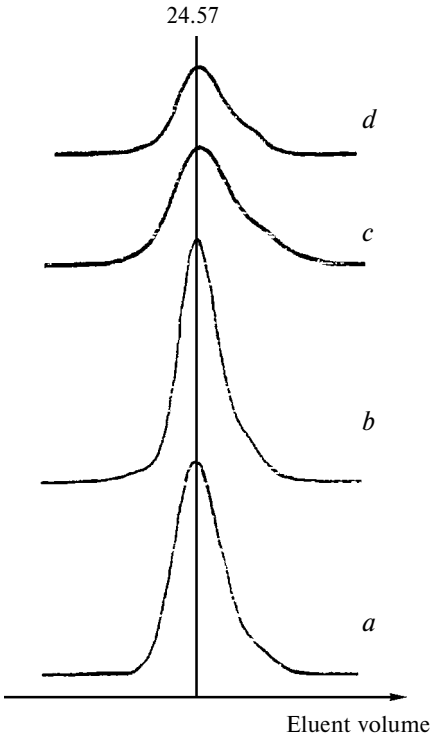

Fig. 4. Chromatograms of the trimethylsilylation products: copper/sodium vinylsiloxane **2a** (*a*); copper chlorovinylsiloxane **3a´** (*b*); copper/sodium methylsiloxane **2b** (*c*), and copper chloromethylsiloxane **3b** (*d*).

Hence, the Si : Cu or Si : Cu : Cl ratio serves as the main characteristic of the compounds synthesized.

Bis(hexaphenylcyclohexasiloxanehexaolato)hexacopper(II) (1). Methanol (70 mL), phenyltriethoxysilane (24.1 g, 0.1 mol), water (3.6 g, 0.2 mol), and sodium (2.3 g, 0.1 mol) were placed in a three-neck flask equipped with a stirrer, a dropping funnel, and a reflux condenser. The reaction mixture was refluxed with stirring for 1 h. Then dioxane (400 mL) was added, the reflux condenser was changed for a direct condenser, and the methanol (70 mL) was distilled off, after which a solution of $CuCl_2$ (6.72 g, 0.05 mol) in methanol (35 mL) was added dropwise, the methanol being continued to distill off. The reaction mixture was refluxed for 6 h and then immediately filtered. The precipitate was washed on a filter with hot dioxane. Compound **1** was isolated from the filtrate in a yield of 12.5 g (64.2%) as turquoise crystals. Found (%): C, 43.09; H, 3.54; Si, 14.51; Cu, 16.36; Si : Cu = 2.01 : 1. $C_{72}H_{60}O_{24}Si_{12}Cu_6$. Calculated (%): C, 42.65; H, 2.98; Si, 16.62; Cu, 18.80; Si : Cu = 2 : 1.

Dodecavinylcyclododecasiloxanedodecaolatooctacopper(II) tetrachloride (3a). Compound **2a** (2.2 g, 1.5 mmol), $CuCl_2$ (0.8 g, 6 mmol), and dioxane (350 mL) were placed in a three-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel, and the reaction mixture was heated to boiling. Then DMSO (15 mL) was added. The reaction mixture was refluxed for 1 h and immediately filtered. The precipitate was washed on a filter with hot dioxane. The crystalline precipitate that formed was recrystallized from a toluene—DMSO mixture. Compound **3a**$\cdot 4Me_2SO \cdot 3C_7H_8$ was isolated in a yield of 2.55 g (73%) as a white crystalline compound. Found (%): C, 24.59; H, 3.61; Si, 14.00; Cu, 21.81; Cl, 5.92; Si : Cu : Cl = 12 : 8.26 : 4.01. $C_{24}H_{36}O_{24}Si_{12}Cu_8Cl_4$. Calculated (%): C, 17.0; H, 2.14; Si, 19.88; Cu, 29.98; Cl, 8.36; Si : Cu : Cl = 12 : 8 : 4.

Dodecamethylcyclododecasiloxanedodecaolatooctacopper(II) tetrachloride (3b). Compound **2b** (2.3 g, 1.62 mmol), $CuCl_2$ (0.87 g, 6.48 mmol), and dioxane (350 mL) were placed in a three-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel. The reaction mixture was heated to boiling. Then DMSO (15 mL) was added. The reaction mixture was refluxed for 15 min and immediately filtered. The precipitate was washed on a filter with hot dioxane. The crystalline precipitate that formed was recrystallized from a toluene—DMSO mixture. Compound **3b** was isolated in a yield of 2.17 g (64%) as a blue crystalline compound. Found (%): C, 15.55; H, 4.42; Si, 16.18; Cu, 24.55; Cl, 6.98; Si : Cu : Cl = 12 : 8.04 : 4.09. $C_{12}H_{36}O_{24}Si_{12}Cu_8Cl_4$. Calculated (%): C, 9.29; H, 2.34; Si, 21.72; Cu, 32.76; Cl, 9.14; Si : Cu : Cl = 12 : 8 : 4.

Trimethylsilylation of organometallasiloxanes (OMS). Trimethylsilylation was carried out according to a procedure described earlier.[7] Organometallasiloxane was added to a mixture of pyridine and trimethylchorosilane (TMCS) in toluene. The reaction mixture was refluxed for 2 h. Then the toluene solution of the cyclosiloxane synthesized was washed until the reaction for Cl^- ions was absent, after which the reaction mixture was concentrated to a constant weight. All the compounds were synthesized as transparent colorless viscous liquids (Table 1).

Dodecavinyldodeca(trimethylsiloxy)cyclododecasiloxane $[CH_2{=}CHSiO(OSiMe_3)]_{12}$ (4a). ^{1}H NMR, δ: 0.20 (s, 9 H, SiMe); 6.30 (br.s, 3 H, $SiCH{=}CH_2$). Found (%): C, 37.53; H, 7.50: Si, 34.62. M_z 1817. $C_{60}H_{144}Si_{24}O_{24}$. Calculated (%): C, 37.55; H, 7.54; Si, 35.05. The molecular weight is 1923.

Dodecamethyldodeca(trimethylsiloxy)cyclododecasiloxane $[MeSiO(OSiMe_3)]_{12}$ (4b). ^{29}Si NMR, δ: 8.06 ($SiMe_3$); −6.85 (SiMe). Found (%): C, 32.37; H, 8.12; Si, 37.87. M_z 1755. $C_{48}H_{144}Si_{24}O_{24}$. Calculated (%): C, 32.39; H, 8.15; Si, 37.87. The molecular weight is 1755.

X-ray diffraction analysis of complex 3a. Crystals ($C_{53}H_{84}Cl_4Cu_8O_{28}S_4Si_{12}$, M = 2284.64) are monoclinic, space

Table 1. Amounts of the starting compounds and yields of cyclosiloxanes

Starting compound	Amount/g (mmol)			Cyclosiloxane	Yield/g (%)
	OMS	TMCS	Pyridine		
2a	1.46 (1.05)	6.86 (63.2)	4.99 (63.2)	$[CH_2{=}CHSiO(OSiMe_3)]_{12}$	1.40 (69)
2b	1.85 (1.50)	9.93 (91)	7.20 (91)	$[MeSiO(OSiMe_3)]_{12}$	2.25 (89)
3a	2.60 (1.53)	10.0 (92)	7.25 (92)	$[CH_2{=}CHSiO(OSiMe_3)]_{12}$	1.60 (76)
3b	2.60 (1.16)	7.55 (69.5)	5.49 (69.5)	$[MeSiO(OSiMe_3)]_{12}$	1.73 (84)

group $P2_1/n$, at T = 110 K, a = 10.734(2), b = 29.539(6), c = 28.020(5) Å, β = 95.712(4)°, V = 8840(3) Å^3, Z = 4, d_{calc} = 1.717 g cm^{-3}, μ = 23.34 cm^{-1}, $F(000)$ = 4632. Intensities of 91968 reflections were measured on an automated Smart CCD 1000 diffractometer (graphite monochromator, λ-Mo-Kα = 0.71073 Å, ω scanning technique, θ_{max} = 28°), of which 21268 independent reflections (R_{int} = 0.0697) were used in the structure refinement. The semiempirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic thermal parameters for all nonhydrogen atoms. Analysis of difference electron density syntheses demonstrated that the copper atoms (Cu(2), Cu(3), Cu(6), and Cu(7)), the oxygen atoms coordinated to the disordered copper atoms, and the Si(1) atom are disordered over two positions with occupancies of 0.6 and 0.4. Disorder was also revealed for some vinyl groups and toluene molecules of solvation. The disordered vinyl groups and toluene molecules were refined with restrictions on the bond lengths (DFIX). The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. The final R factors are as follows: R_1 = 0.0545 (against F for 12309 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.1482, GOOF = 1.091, 882 parameters were refined. Calculations were carried out using the SHELXTL PLUS program package.

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