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Metallosiloxanes with Acetylacetonate Ligands

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Abstract—The reactions of neutral cage metallophenylsiloxanes $[PhSiO_2]_6M_6[PhSiO_2]_6$ (M = Cu or Ni) of the sandwich type with alkaline acetylacetonate K(Acac) and of alkaline cage metallosiloxane $[PhSiO_2]_{12}Cu_4Na_4$ of the globular type with the neutral complex $Co(Acac)_2$ are studied. Hexanuclear Cu_6- (**I**) and Ni_6-phenylsiloxanes (**II**) and octanuclear (Cu_4,Co_4)-phenylsiloxane (**III**) formed in the reactions are studied by X-ray diffraction analysis (CIF files CCDC nos. 1974285 (**I**), 1974286 (**II**), and 1974287 (**III**)). It is shown that the type of the structure (sandwich or globular) of the initial metallosiloxane is retained in all cases. However, in the case of Ni-siloxane, the coordination with two Acac ligands results in an appreciable shift of the siloxane cycles relative to each other and in the transformation of the usual sandwich characteristic of neutral Ni-phenylsiloxane into a distorted sandwich. The presence of four Acac ligands in globular (Cu_4,Co_4)-phenylsiloxane lead to the elongation of the distance between two linear Cu–Cu fragments of the molecules, which provides the formation of the structure of the "biconvex lens" type.

Keywords: metallosiloxanes, bimetallic compounds, cage copper- and nickelphenylsiloxanes, sandwich and globular metal complexes, potassium and cobalt(II) acetylacetonates, X-ray diffraction analysis

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INTRODUCTION

Compounds consisting of transition metals and macrocyclic siloxanolate ligands have a unique ability to form structures of various shapes, which makes it possible to compare them with such classes as polyoxometallates [1, 2] or metal carboxylates [3]. Among metallosiloxanes a special role is played by the complexes synthesized in the reactions of transition metal (Cu, Co, Ni, Cr) halides and oligomeric products of the alkaline hydrolysis of organotriethoxysilanes of the general formula $(M[RSiO_2])_n$ in media of polar organic solvents characterized by the electron-donor ability [4, 5]. These metallosiloxanes can be classified as two main structural types: sandwich and globular (or saddle). This classification mainly concerns the number and nature of siloxanolate ligands. Sandwich metallosiloxanes are known for such metals as copper, nickel, cobalt, and chromium, whereas globular metallosiloxanes are known for copper only. Both types of the structures allow one to control the shape of both types of structures can be controlled by changing the nature of the transition metal and their ligand environment [6–8]. The magnetochemical [9–12] and catalytic [13, 14] properties were studied for some sandwich and globular metallosiloxanes, and were shown to be mainly controlled by the cage structure.

Sandwich metallosiloxanes consist of an even number of transition metals, namely, 4, 6, 8, or 10 (pentanickelsiloxane [12] and pentacoppersiloxane [15] are exceptions), and two macrocyclic siloxane ligands. Sodium or potassium atoms can be included in the structure of the metallosiloxane cage. According to the published data, the shape of the metallosiloxane sandwich cage is close to the cylindrical one. Another shape of the metallosiloxane cage is also possible, which is characterized by the violation of the cylindrical symmetry in such a way that the angle between the straight line connecting centroids of two siloxanolate ligands and the perpendicular put from the centroid of one of the siloxanolate ligands onto the mean plane of another ligands is lower than 90°. The shape of this type resembles a distorted cylinder (distorted sandwich). The oxygen atoms corresponding to the hydroxyl or O^{2-} groups are localized inside the cage of this type. The structure of the distorted sandwich type was obtained only for several compounds of octa- and tetranuclear nickelsiloxanes [16, 17], tetranuclear cadmiumsiloxane [18], and binuclear chromiumsiloxane [19]. Another type of deformation was found for the transmetallation of cage coppersiloxanes of the $[RSiO_2]_6Na_4Cu_4[RSiO_2]_6$ type. The replacement of sodium atoms by alkaline-earth metal atoms with a longer ionic radius (for example, strontium or barium [6]) results in the formation of metallosiloxane cages with the shape of an oblate cylinder. It should be mentioned that the distortion increases with an increase in the ionic radius of the metal. One more type of distortion of the cylindrical structure of the metallosiloxane fragment is observed in the case where a series of metal atoms is additionally coordinated by the bipyridyl and hydroxyl group [20]. The addition of bipyridine during the synthesis of the complex exerts a direct effect, most likely, on the structure of the formed product. As a result, the metallosiloxane fragment becomes more "flattened" than that formed in the case of the insertion of alkaline-earth metals, so that the single metal–oxide belt (named the "quantum ring" [11]) is cleaved into two nearly linear copper-containing fragments (for example, in coppersiloxane with the methyl-2-amino-2-oxo-*N*,*N*'-ethanimidoate ligand [21]). The terminal copper atoms of these fragments are involved in weak coordination interactions with the oxygen atoms of the adjacent copper-containing fragment.

The globular type structure includes one twelve-unit ligand of a complicated shape, four copper atoms, and four alkaline metal atoms. The shape of the metallosiloxane cage of this type changes when the nature of the alkaline metal is varied or the alkaline metal is replaced by any transition metal. We showed that the replacement of the sodium atom by lithium resulted in the shortening of the interatomic distance between the oppositely lying copper atoms and oxygen atoms of two linear mutually perpendicular metal-containing fragments. Thus, the metallosiloxane fragment takes the shape of a biconcave lens. On the contrary, the replacement of sodium by potassium leads to the biconvex lens shape [7].

All earlier studied metal exchange reactions are within traditional concepts of the metallosiloxane chemistry: replacement of the alkaline metal atom in the SiOM group by the exchange reaction with the corresponding metal halide $MHal_2$.

The purpose of this work is to study possibilities of the metal exchange involving metal acetylacetonates and the influence of chelate organic ligands on the structure of cage metallosiloxanes.

EXPERIMENTAL

The syntheses were carried out in air. Butanol, tetrahydrofuran (THF), dioxane, toluene, pyridine, anhydrous ethanol, and chloroform were purified using standard procedures [22]. Potassium and cobalt acetylacetonates were commercially available (ACRUS) and used as received. Copperphenylsiloxane, nickelphenylsiloxane, and coppersodiumphenylsiloxane were synthesized using known procedures [23, 24].

Reaction of $[PhSiO_2]_6Cu_6[PhSiO_2]_6$ with K(Acac). Potassium acetylacetonate trihydrate $K(Acac)\cdot 3H_2O$ (3.75 g, 19.27 mmol) was dissolved in anhydrous ethanol (50 mL), and cage copperphenylsiloxane $[PhSiO_2]_6Cu_6[PhSiO_2]_6$ (3.88 g, 1.62 mmol) was added. After a week, a blue-violet crystalline precipitate with insertions of turquoise crystals of compound **I** was formed. The crystals of compound **I** suitable for X-ray diffraction analysis (XRD) were mechanically separated from the precipitate. The remained precipitate was filtered off, washed with ethanol from potassium acetylacetonate residues and with chloroform from copper acetylacetonate, and dried in air to a constant weight. Blue-violet crystalline copperpotassiumphenylsiloxane was obtained by the recrystallization of the precipitate from butanol in a yield of 2.50 g (70.5%).

For $\{[PhSiO_2]_6\}_2Cu_4K_4$

Anal. calcd., %	Si, 16.34	Cu, 12.38	K, 7.61 (ratio Si : Cu : K = 3 : 1 : 1)
Found, %	Si, 14.28	Cu, 12.30	K, 8.78 (ratio Si : Cu : K = 3.0 : 1.15 : 1.30)

Reaction of $[PhSiO_2]_6Ni_6[PhSiO_2]_6$ with K(Acac). Potassium acetylacetonate monohydrate $K(Acac)\cdot H_2O$ (2.43 g, 15.76 mmol) was dissolved in anhydrous ethanol (60 mL), and nickelphenylsiloxane $[PhSiO_2]_6Ni_6[PhSiO_2]_6$ (3.21 g, 1.31 mmol) was added to the resulting solution. The mixture was stirred for 24 h, and toluene (30 mL) was added. After 8 days, the reaction mixture was filtered from mixed nickel and potassium acetylacetonate. Yellow-green crystals were isolated from the partially evaporated filtrate and recrystallized from butanol to obtain yellow crystals of compound **II** in a yield of 0.65 g (16.6%). Found, %: Si, 11.28; Ni, 11.9; K, 2.6 (ratio Si : Ni : K = 12.0 : 6.06 : 1.99).

The evaporation of the remained mother liquor to dryness from an ethanol–toluene (2 : 1) mixture gave yellow polymeric metallosiloxane in a yield of 3.02 g (81.2%). Found, %: Si, 11.90; Ni, 2.35; K, 14.45 (ratio Si : Ni : K = 12.0 : 1.13 : 10.50).

Reaction of $[PhSiO_2]_{12}Cu_4Na_4$ with $Co(Acac)_2\cdot 2C_2H_5OH$. A solution of $Co(Acac)_2\cdot 2C_2H_5OH$ (0.7 g, 2 mmol) in THF (20 mL) was added to a suspension of $[PhSiO_2]_{12}Cu_4Na_4$ (1.08 g, 0.5 mmol) in THF (20 mL). The mixture was stirred at room temperature for 2 h and then refluxed for 1 h. A pink precipitate was filtered off and washed with chloroform, and the filtrate was evaporated. A blue-lilac resin was formed in a yield of 0.8 g (75%). Found, %: Si, 11.13; Cu, 8.4; Co, 4.25; Na, 1.25 (ratio Si : Cu : Co : Na = 12.0 : 4.0 :

2.17 : 1.64). An insignificant amount of crystals of compound **III** was isolated from a solution of the resin in a dioxane–pyridine (4 : 1) mixture.

Metalloorganosiloxanes were trimethylsilylated using a known procedure [25].

XRD. The crystals of compound **I** were isolated from an ethanol solution, the crystals of compound **II** were grown by recrystallization from butanol, and the crystals of compound **III** were isolated from a dioxane–pyridine (4 : 1) mixture. The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for F_{hkl}^2. In the structure of compound **I**, one of the potassium atoms (K(1)) and the most part of phenyl substituents at the silicon atoms and coordination ethanol molecules are disordered. To refine these fragments, the restraints imposed on their geometry, in particular, bond lengths (DFIX and AFIX 66 rules), were used. Some ethanol molecules are disordered around the crystallographic inversion center. It was rather difficult to refine the latter and, hence, their geometry was specified as a rigid fragment with the 50% population to provide the stability of the least squares (the geometry and isotropic shift factors were fixed). The disordering of some phenyl substituents and coordination pyridine molecules was also revealed in the structure of compound **III** (the refinement was carried out similarly to the structure of compound **I**). In addition, one of the cobalt atoms (Co(4)) and its coordination environment are also disordered in a ratio of 2 : 3. Hydrogen atoms were calculated from the geometric concepts and included into refinement with the fixed C–H and O–H distances and with restraints imposed on their equivalent shift parameters. Positions of the hydrogen atoms of the hydroxyl groups were neither revealed, nor calculated for a series of coordinated ethanol and butanol molecules. It is most likely that the disordering of many molecular fragments was a reason for a weak intensity of the diffraction pattern at the angles 2θ° > 40° and did not allow one to reach low divergence parameters for compounds **I** and **II**.

All calculations were performed using the SHELXL [26] and OLEX2 [27] programs. Selected crystallographic data and structure refinement parameters for compounds **I**–**III** are presented in Table 1.

The coordinates of atoms and other parameters of compounds **I**–**III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1974285–1974287, respectively; deposit@ccdc.cam.ac.uk or https://www.ccdc.cam.ac.uk).

^{1}H NMR spectra were recorded on a Bruker Avance TM 400 MHz spectrometer (Germany) with a working frequency (for ^{1}H) of 400.13 MHz. Solutions in $CDCl_3$ and in acetone-d_6 were used, chemical shifts were measured relative to tetramethylsilane, and the spectra were recorded at $T = 298$ K.

RESULTS AND DISCUSSION

It is known that the depth of the reactions of cage metallosiloxanes with acetylacetone is determined by a comparative stability of the acetylacetonate complexes and metallosiloxanes [28]. For example, in the case of copperphenylsiloxane $[PhSiO_2]_6Cu_6[PhSiO_2]_6$, the cleavage occurs with a nearly quantitative yield of hexaphenylhexahydroxycyclohexasiloxane $[PhSiO(OH)]_6$ (Hexol), whereas for similar manganesesiloxane an insignificant amount of siloxanol can be isolated only in the presence of high acetylacetone excess. In this case, the backward reaction takes place: the known cage manganesephenylsiloxane is formed by the reaction of Hexol with manganese acetylacetonate. We assumed that an exchange between the siloxanolate and acetylacetonate ligands is possible in metallosiloxane–metal acetylacetonate systems, and the direction of the ligand exchange would be determined by the ratio of the stability constants of the initial and formed metal complexes. Favorable conditions for the ligand exchange are observed when the acetylacetonate complex of the metal, which enters into the metalloorganosiloxane composition, is more stable. The stability of the acetylacetonate complexes $M(Acac)_2$ varies in wide ranges ($\log K_1$ for Cu, Ni, and Co(II) is 11.85, 9.70, and 7.81, respectively; for potassium, $\log\beta = 2.1$) [29].

It was assumed that the reactions of cage metallophenylsiloxanes with sodium or potassium acetylacetonates would involve the complete substitution of the transition metal atoms in the metallosiloxane by the alkaline metal atoms of the acetylacetonate complex, which would result in the formation of sodium and potassium phenylsilanolates via the following scheme:

$$[PhSiO_2]_6M_6[PhSiO_2]_6 \xrightarrow[-M(Acac)_2]{KAcac} [PhSiOOK]_n.$$

Therefore, the sandwich copper- and nickelphenylsiloxanes–potassium acetylacetonate and saddle (copper, sodium)phenylsiloxane–cobalt(II) acetylacetonate systems were chosen as the main objects of the study.

It was found for the copperphenylsiloxane–potassium acetylacetonate system that at the ratio copperphenylsiloxane : K(Acac) = 1 : 12 the major reaction product is the already known copperpotassiumphenylsiloxane of the sandwich structure: $[PhSiO_2]_6K_4Cu_4[PhSiO_2]_6$ [28]; i.e., in fact the reaction proceeds via the following scheme:

$$[PhSiO_2]_6Cu_6[PhSiO_2]_6$$
$$\xrightarrow[-Cu(Acac)_2]{KAcac} [PhSiO_2]_6Cu_4K_4[PhSiO_2]_6.$$

An insignificant amount of turquoise crystals were observed along with the above compound. Their study by the XRD method showed that the compound corresponded to the formula $\{[PhSiO_2]_6\}_2Cu_6K_2(Acac)_2$ (compound **I**).

Table 1. Selected crystallographic data and structure refinement parameters for compounds **I**, **II**, and **III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{139.32}H_{147.62}O_{36.32}Si_{12}K_2Cu_6$	$C_{125.34}H_{187.34}O_{44.67}Si_{12}K_4Ni_6$	$C_{107.49}H_{103.28}N_3O_{32}Si_1Co_4Cu_{42}$
Diffractometer	Bruker Smart 1000	Bruker Smart 1000	Bruker APEX II
Radiation (λ, Å)	MoK_α (0.71073)		
FW	3199.67	3222.26	2776.99
T, K	100	120	100
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	1	2	4
a, Å	14.6266(11)	17.1989(8)	28.547(2)
b, Å	14.8467(12)	16.8936(8)	16.1174(12)
c, Å	17.3370(12)	27.5106(13)	29.771(2)
α, deg	93.146(2)	90	90
β, deg	97.1640(10)	97.4130(10)	103.698(2)
γ, deg	96.785(2)	90	90
V, Å^3	3700.0(5)	7926.4(6)	13308.1(17)
ρ_{calc}, g cm^{-3}	1.436	1.350	1.386
μ, cm^{-1}	10.75	9.21	12.89
F(000)	1654	3385	5671
$2\theta_{max}$, deg	52.04	52.04	52.04
Number of measured reflections	16621	46169	118263
Number of independent reflections	14187	15540	26220
Number of reflections with $I > 2\sigma(I)$	10271	8239	12650
Number of refined parameters	853	549	1179
R_1 ($I > 2\sigma(I)$)	0.0525	0.1044	0.0929
wR_2	0.1589	0.3333	0.2753
GOOF	1.039	0.949	1.060
Residual electron density (max/min), e Å^{-3}	1.436/–0.939	1.76/–2.09	1.237/–2.129

The structure of compound **I** (Fig. 1) can be described by a sandwich complex, but the closed metal–oxide belt is absent. Two metal–oxide fragments containing three copper atoms each are observed instead of the belt in compound **I**. In each fragment, the terminal copper atoms are linked with the acetylacetonate ligand. The Cu...Cu interatomic distance in these fragments is 2.93 Å on the average. Two oxygen atoms corresponding to the coordinated water molecules are localized inside the complex, which is indicated by the shortened O(7)...O(7) distance (–*x*, –*y*, –*z*; 1.874(4) Å). No hydrogen atoms of these water molecules were revealed. The main bond lengths of compound **I** are presented in Table 2.

For the reaction of nickelphenylsiloxane with potassium acetylacetonate at the same ratios, the major reaction product (81%) is the polymer with the ratio Si : Ni : K = 12 : 1.1 : 10.5. The method of destructive trimethylsilylation combined with ^{1}H NMR spectroscopy was used to study the structure of the polymer synthesized by the reaction of nickelphenylsiloxane with potassium acetylacetonate.

It is known that the reactions of trimethylchlorosilane with metalloorganosiloxanes in the presence of pyridine involve the cleavage of the Si–O–M bonds and formation of the corresponding trimethylsilyl derivatives with the retention of the skeleton of the siloxane fragments of metalloorganosiloxane [25]. For

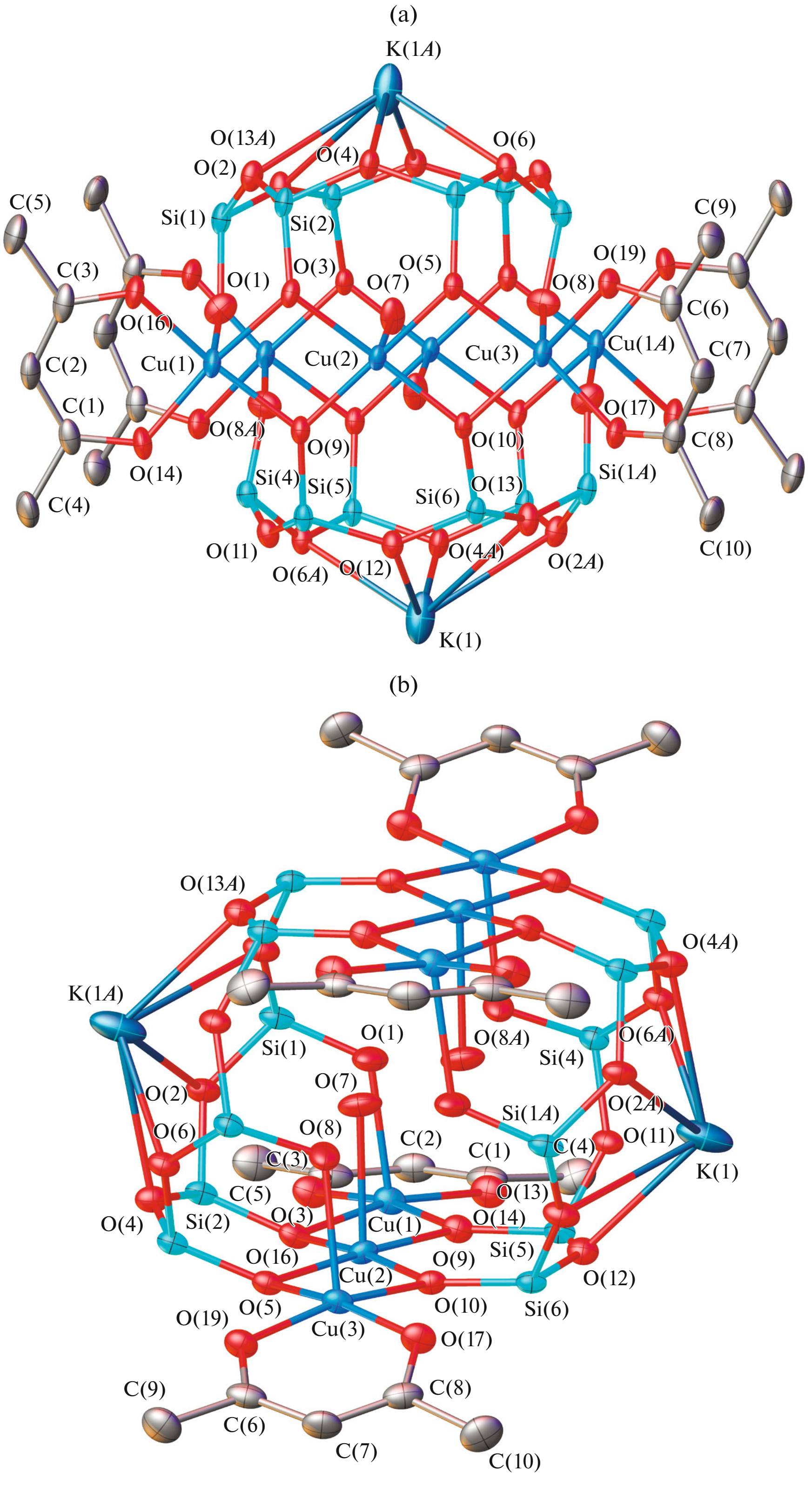
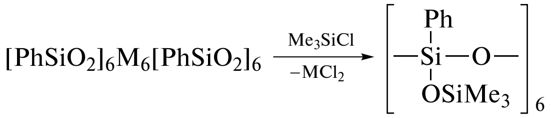


Fig. 1. (a) Side view and (b) view from above of the metallosiloxane fragment of complex **I**. Hydrogen atoms and phenyl groups at the silicon atoms are omitted. Symmetry transform: (*A*) 2 – *x*, 2 – *y*, –*z*.

Table 2. Selected bond lengths in the structure of compound **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	2.282(3)	Cu(2)–O(9)	1.946(3)
Cu(1)–O(3)	1.991(3)	Cu(2)–O(10)	1.933(3)
Cu(1)–O(9)	1.960(3)	Cu(3)–O(5)	1.987(3)
Cu(1)–O(14)	1.912(3)	Cu(3)–O(8)	2.307(3)
Cu(1)–O(16)	1.907(3)	Cu(3)–O(10)	1.953(3)
Cu(2)–O(3)	1.936(3)	Cu(3)–O(17)	1.915(3)
Cu(2)–O(5)	1.959(3)	Cu(3)–O(19)	1.915(3)
Cu(2)–O(7)	2.388(6)	K–O (average)	2.960(10)

sandwich metallosiloxane, this reaction is described by the following scheme:



$$[PhSiO_2]_6M_6[PhSiO_2]_6 \xrightarrow[-MCl_2]{Me_3SiCl} \left[-\overset{Ph}{\underset{OSiMe_3}{Si}}-O- \right]_6$$

The ^{1}H NMR spectrum of the product synthesized by polymer trimethylsilylation is presented in Fig. 2. The spectrum of model hexaphenylhexa(trimethylsiloxy)cyclohexasiloxane formed by the trimethylsilylation of the starting sandwich nickelphenylsiloxane is presented for comparison in Fig. 3.

In the case of the polymer, the ^{1}H NMR spectrum exhibits broad signals in the ranges of protons of the methyl groups at silicon and protons of the phenyl substituent; i.e., polymer formation is accompanied by a substantial rearrangement of the siloxane cage.

The product (16.6% yield) with the ratio Si : Ni : K = 12 : 6.06 : 1.99 was isolated along with the polymer. The XRD data indicate that the crystalline mass contains compound **II** with chelate ligands and four potassium atoms.

The metallosiloxane cage of compound **II** (Fig. 4) occupies the crystallographic inversion center and corresponds, on the whole, to the "distorted sandwich" structure similarly to the earlier studied nickel- and cadmiumsiloxanes. Two oxygen atoms corresponding to the hydroxyl groups are localized inside the metallosiloxane cage. Two potassium atoms (K(1) and K(1*A*)) are coordinated by the siloxanolate oxygen atoms, whereas other two atoms (K(3) and K(3*A*)) are bound to the oxygen atoms of the siloxane cycles.

The coordination polyhedra of the majority of nickel atoms correspond to a distorted octahedron. The Ni(2) and Ni(2*A*) atoms are coordinated only by the siloxanolate ligands $[PhSiO_2]_6$ and inner-cage hydroxyl anions. In turn, the Ni(3) and Ni(3*A*) atoms form only five bonds with the aforementioned fragments, and the sixth bond in the octahedron is formed due to the coordination with the butanol molecule. The acetylacetonate ligands are linked with the Ni(1)

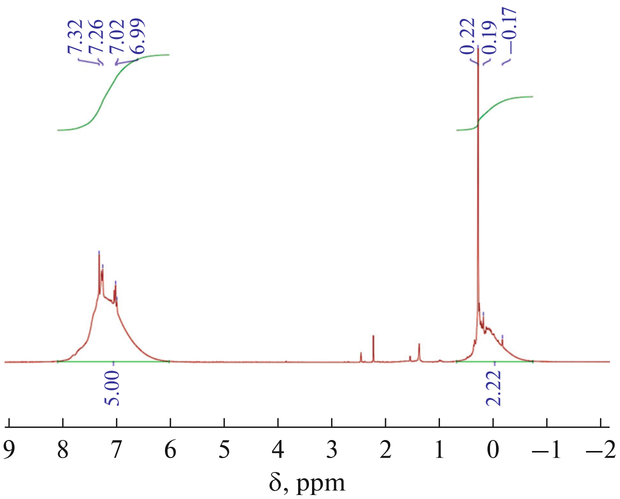


Fig. 2. ^{1}H NMR spectrum of the trimethylsilylation product of the polymer synthesized by the reaction of sandwich nickelphenylsiloxane with potassium acetylacetone.

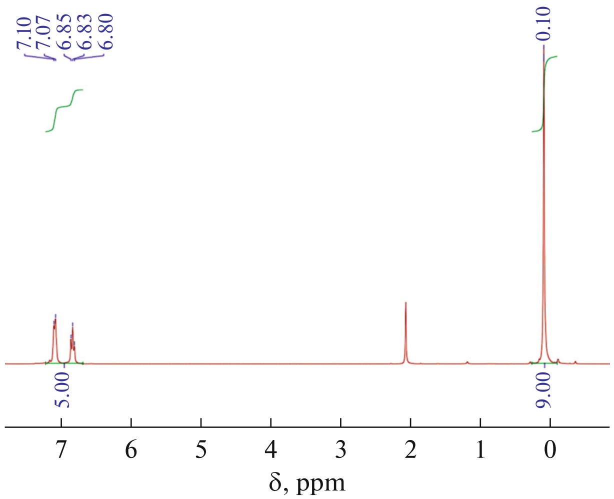


Fig. 3. ^{1}H NMR spectrum of hexaphenyl(hexatrimethylsiloxy)cyclohexasiloxane synthesized by the trimethylsilylation of sandwich nickelphenylsiloxane.

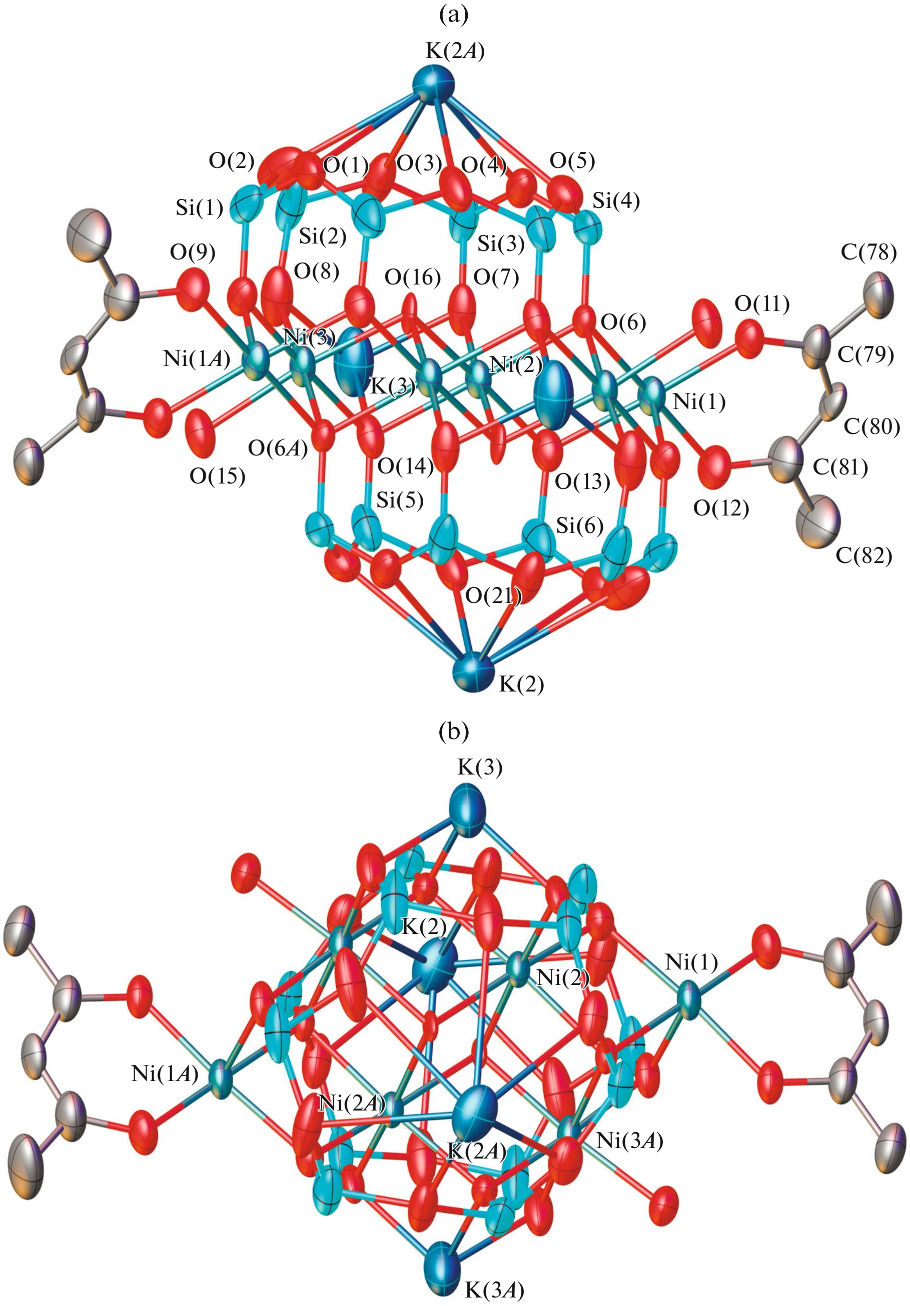


Fig. 4. (a) Side view and (b) view from above of the metallosiloxane fragment of complex **II**. Hydrogen atoms and phenyl groups at the silicon atoms are omitted. Symmetry transform: (*A*) 2 – *x*, 2 – *y*, –*z*.

and Ni(1*A*) atoms, and other bonds are formed due to the coordination with the butanol molecules and siloxanolate ligands $[PhSiO_2]_6$. The inner-cage hydroxyl group (O(16)) is bound to three nickel atoms, and the Ni(3)–O(16), Ni(2)–O(16), and Ni(2*A*)–O(16) bond lengths vary in a range of 2.09–2.15 Å, which is close to the values for the earlier described nickelsiloxanes of this type.

The interatomic distances Ni...Ni in compound **II** vary in a fairly broad range (3.075–3.145 Å). The Ni(1)...Ni(2) and Ni...Ni(3*A*) distances involving the Ni(1) atom linked with the acetylacetonate ligands are appreciably shorter (3.075 Å) than those in the case of the nickel atoms that are not linked with the ligands. Selected bond lengths and bond angles in compound **II** are presented in Table 3.

Rather unusual result was obtained for the reaction of cobalt acetylacetonate with globular coppersodiumphenylsiloxane. An analysis of the polymer formed showed all the three metals in its composition (ratio

Table 3. Selected bond lengths and bond angles in the structure of compound **II**

Bond	*d*, Å	Bond	*d*, Å
Ni(1)–O(6)	2.127(4)	Ni(2)–O(16)	2.100(4)
Ni(1)–O(11)	2.020(4)	Ni(2)–O(16*A*)	2.145(4)
Ni(1)–O(12)	2.010(5)	Ni(3)–O(15)	2.111(5)
Ni(1)–O(10)	2.093(4)	Ni(3)–O(6*A*)	2.136(4)
Ni(1)–O(13)	2.057(4)	Ni(3)–O(9*A*)	2.041(4)
Ni(1)–O(9*A*)	2.037(4)	Ni(3)–O(16)	2.093(3)
Ni(2)–O(6)	2.145(4)	Ni(3)–O(8)	2.092(5)
Ni(2)–O(7)	2.078(4)	Ni(3)–O(9)	2.032(4)
Ni(2)–O(13)	2.038(5)	Ni(3)–O(14)	2.098(4)
Ni(2)–O(14)	2.133(4)	K–O (average)	2.773(8)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(11)Ni(1)O(12)	89.9(2)	O(11)Ni(1)O(13)	175.7(2)
Ni(2)O(16)Ni(3)	97.3(2)	O(12)Ni(1)O(6)	179.5(2)
Ni(2)O(16)Ni(2*A*)	98.98(14)	O(15)Ni(3)O(16*A*)	170.5(2)

Si : Cu : Co : Na = 12 : 4 : 2.17 : 1.64). As in the case of nickelsiloxane, the siloxane skeleton of the molecule is rearranged during the reaction, which is indicated by the ^{1}H NMR spectrum of the product of polymer trimethylsilylation (Fig. 5). The spectrum of dodecaphenyl(dodecatrimethylsiloxy)cyclododecasiloxane synthesized by the trimethylsilylation of the starting globular coppersodiumphenylsiloxane is shown for comparison (Fig. 6). However, an insignificant amount of compound **III** was isolated from a solution of this polymer in a dioxane–pyridine (4 : 1) mixture. According to the XRD data, compound **III** corresponds to the formula $[PhSiO_2]_{12}Cu_4Co_4(Acac)_4$ (Fig. 7). In this case, sodium is replaced by the –Co(Acac) group.

Compound **III** contains four copper atoms and four cobalt atoms linked with four acetylacetonate ligands (Fig. 7). Thus, this compound is the first example of metallosiloxanes with the “saddle” structure containing eight atoms of transition metals of various nature. It should be mentioned that the single examples of metallosiloxanes containing transition metals of different types are the sandwich complexes of divalent iron and nickel [30, 31]. It has previously been shown [32] that two types of structures with the shapes of “biconvex” and “biconcave” lenses (the dis-

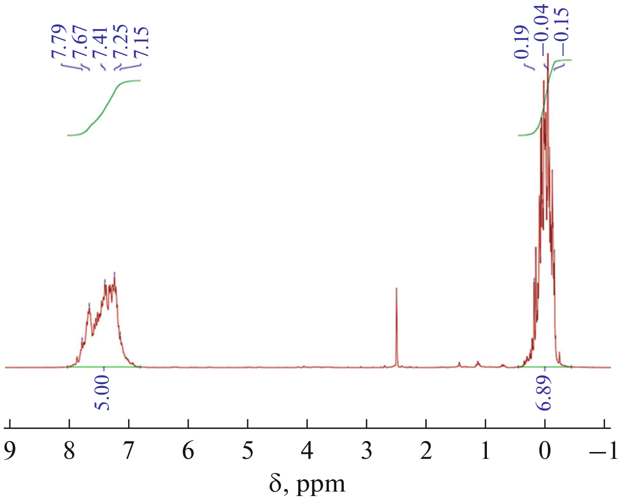


Fig. 5. ^{1}H NMR spectrum of the trimethylsilylation product of the polymer synthesized by the reaction of globular coppersodiumphenylsiloxane with cobalt acetylacetone.

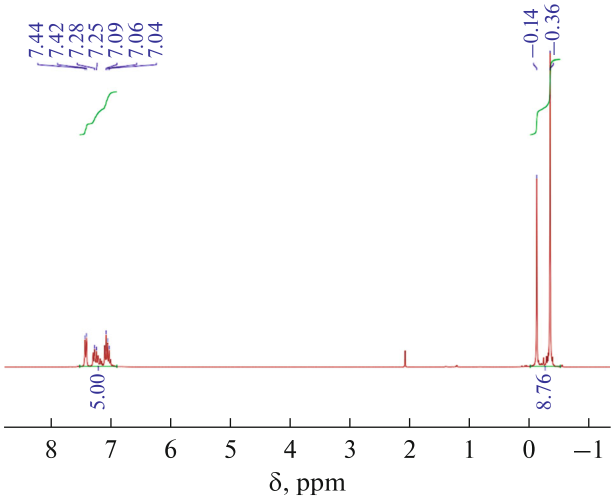


Fig. 6. ^{1}H NMR spectrum of dodecaphenyl(dodecatrimethylsiloxy)cyclododecasiloxane synthesized by the trimethylsilylation of the initial globular coppersodiumphenylsiloxane.

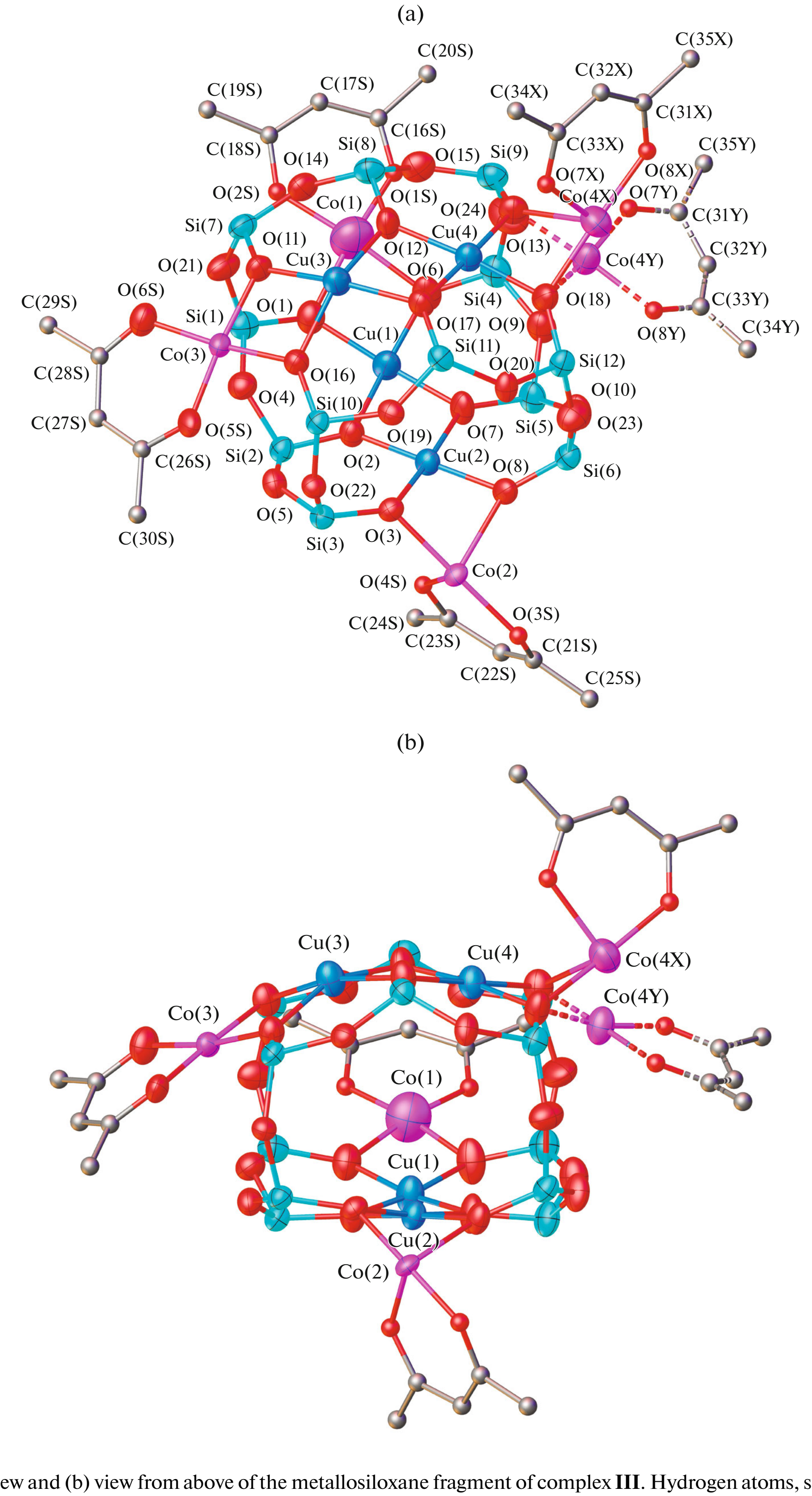


Fig. 7. (a) Side view and (b) view from above of the metallosiloxane fragment of complex **III**. Hydrogen atoms, some coordination pyridine molecules, and phenyl groups at the silicon atoms are omitted. One of the Co(Acac) fragments is disordered, and the corresponding positions designated as (Y) are shown by dash.

Table 4. Selected bond lengths and bond angles in the structure of compound **III**

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	2.035(5)	Cu(1)–O(6)	1.943(5)
Co(1)–O(6)	2.035(5)	Cu(3)–O(11)	2.031(4)
Co(1)–O(1S)	1.823(5)	Cu(3)–O(12)	1.987(5)
Co(1)–O(2S)	1.935(6)	Cu(3)–O(16)	2.004(4)
Co(2)–O(3)	2.016(4)	Cu(3)–O(17)	2.018(4)
Co(2)–O(8)	2.199(4)	Cu(4)–O(12)	1.946(4)
Co(2)–O(3S)	1.922(4)	Cu(4)–O(13)	1.950(4)
Co(2)–O(4S)	1.952(5)	Cu(4)–O(17)	1.970(4)
Co(3)–O(11)	1.952(4)	Cu(4)–O(18)	1.905(5)
Co(3)–O(16)	1.943(4)	Co(4Y)–O(13)	1.919(5)
Co(3)–O(5S)	1.902(5)	Co(4Y)–O(18)	1.991(5)
Co(3)–O(6S)	1.917(5)	Co(4Y)–O(7Y)	1.943(6)
Co(4X)–O(18)	2.011(5)	Co(4Y)–O(8Y)	1.860(5)
Co(4X)–O(8X)	1.906(7)	Cu(1)–O(7)	1.971(4)
Co(4X)–O(7X)	2.067(8)	Cu(2)–O(2)	1.955(4)
Co(4X)–N(4)	2.014(8)	Cu(2)–O(3)	1.939(4)
Cu(1)–O(1)	1.971(5)	Cu(2)–O(7)	1.937(4)
Cu(1)–O(2)	1.960(4)	Cu(2)–O(8)	1.938(4)
Angle	ω, deg	Angle	ω, deg
CoOCu (average)	93.2(2)	CuOCu (average)	98.7(2)

tances between the copper atoms and opposite oxygen atoms are longer than 3.5 Å and shorter than 2.8 Å, respectively) are formed in the case of the octanuclear metallosiloxanes with the Cu–Hal bond. Their superposition is observed in the crystal. In the case of the structure of compound **III**, in spite of cobalt atom (Co(4)) disordering, we can assert that no structures of two types are formed and the formed metallosiloxane has the shape of a "biconvex lens" only (interatomic distances Cu(1)...O(12) and Cu(2)...O(17) are 4.957(5) and 5.080(5) Å, respectively).

The interatomic distances Cu(1)...Cu(2) and Cu(3)...Cu(4) are 2.9585(11) and 3.0029(13) Å, respectively. The distances between the copper and cobalt atoms vary in fairly wide ranges of 2.84–2.98 Å. This indicates that an exchange interaction involving the bridging oxygen atoms of the siloxanolate ligands can occur between transition metals. Selected bond lengths and bond angles in compound **III** are listed in Table 4.

Thus, it was found that the substitution of the transition metal by potassium occurs during the interaction of potassium acetylacetonate with cage copper- and nickelphenylsiloxanes. The structures of the formed compounds are determined by the nature of the transition metal. In the case of saddle coppersodiumphenylsiloxane, sodium atoms can be replaced by cobalt with the acetylacetonate ligand.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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