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Replacement of Ligands in a Molecule of Polyhedral Phenylmetallosiloxane Containing Nickel and Sodium Ions

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Abstract—The possibility of the partial or complete substitution of the outer-sphere solvate shell of *n*-butanol molecules by the nitrogen-containing compounds in the phenylnickelsodiumsiloxane complex. The high-symmetry spatially fixed rigidly cationic layer retains its structure. The obtained complexes $Na_2(\mu\text{-}H_2O)_2(n\text{-BuOH})_2\{[C_6H_5SiO_2]_6Ni_4Na_4(\mu_3\text{-OH})_2[C_6H_5SiO_2]_6\} \cdot 8(n\text{-BuOH}) \cdot 2NH_3$ (**II**) and $\{[C_6H_5SiO_2]_6Ni_4Na_6(\mu_3\text{-OH})_2[C_6H_5SiO_2]_6\} \cdot 4(\mu\text{-}C_3H_7NO) \cdot 6(C_3H_7NO) \cdot 2.8(H_2O) \cdot 0.6(C_3H_7NO)$ (**III**) are studied by X-ray diffraction analysis (CIF files CCDC nos. 1810736 (**II**) and 1810737 (**III**)).

Keywords: organometallasiloxanes, template synthesis, replacement of ligands, X-ray diffraction analysis

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INTRODUCTION

Organometallasiloxanes are compounds molecules of which contain the Si–O–M group, where M^{n+} is the alkaline, transition, or rare-earth metal ion ($n = 1$, 2, and 3). This fairly large class of compounds occupies an intermediate place between siloxanes and silicates. Compounds of mono-, di-, and trifunctional silicon are used for the synthesis of organometallasiloxanes. A combination with various metal ions provides a diversity of structural forms of molecules of the organometallasiloxanes formed [1–8]: from simple and dimeric molecules to cyclic structures [9–14], complicated spirocycles, and polyhedra [15–24]. The polyhedral organometallasiloxanes first obtained in our research group [25–33] play a special role, since their structures differ from those of all other organometallasiloxanes. Their molecules consist of one or two stereoregular organosiloxanolate ligands coordinated to the complex matrix consisting of ions of alkaline (Na^+, K^+) and/or transition metals and lanthanides [34]. The self-assembling of these molecules occurs in the course of the hydrolytic condensation of trifunctional organoalkoxysilanes in the presence of the corresponding metal ions serving simultaneously as a template and structural unit [35–40]. The coordination saturation of the metal ions forming the matrix framework is achieved due to solvate molecules of coordinating solvents in the medium of which the self-assembling of polyhedral organometallasiloxanes occurs. Organometallasiloxanes containing simultaneously transition and alkaline metal ions are of special interest. In particular, this is caused by the ability of these compounds to undergo various framework rearrangements depending on the donor and coordinating properties of the solvate environment.

We have previously shown for the globular phenylcoppersodium siloxane complex that its recrystallization in *N*,*N*-dimethylformamide (DMF) in the presence of bipyridyl results in the rearrangement to a molecule of the sandwich structure containing no alkaline metal ions [41].

Continuing these studies, we studied the reactions of the phenylnickelsodiumsiloxane complex $Na_2\{[C_6H_5SiO_2]_6Ni_4Na_4(\mu_3\text{-OH})_2[C_6H_5SiO_2]_6\} \cdot 16(n\text{-BuOH})$ (**I**) obtained by a described procedure [34] with such nitrogen-containing compounds as ammonia and DMF.

EXPERIMENTAL

All solvents were purified prior to use according to earlier described procedures [42]. Phenyltriethoxysilane, *n*-butanol, DMF, and NaOH were purchased from Acros Organics. Complex **I** was synthesized according to a previously described procedure [34]. The structural parameters of complex **I** were described [26].

Synthesis of complex $Na_2\{[C_6H_5SiO_2]_6Ni_4Na_4(\mu_3\text{-}OH)_2[C_6H_5SiO_2]_6\} \cdot 8(n\text{-}BuOH) \cdot 2NH_3$ (IIa). Gaseous ammonia was passed for 12 h through a solution of compound **I** (0.50 g, 0.214 mmol) in a mixture of toluene (20 mL) and ethanol (3 mL). Green crystals precipitated on the next day were filtered off and dried. The yield of complex **IIa** was 0.38 g (66.6%). A single crystal suitable for X-ray diffraction analysis was selected from the solution. Elemental analysis was carried out for the dried crystals.

For $C_{104}H_{148}N_2O_{34}Si_{12}Na_6Ni_4$

Anal. calcd., % C, 46.89 H, 5.60 N, 1.05 Na, 5.18 Ni, 8.81 Si, 12.65

Found, % C, 45.91 H, 5.73 N, 1.12 Na, 4.93 Ni, 8.40 Si, 12.84

Synthesis of complex $\{[C_6H_5SiO_2]_6Ni_4Na_6(\mu_3\text{-}OH)_2[C_6H_5SiO_2]_6\} \cdot 10(C_3H_7NO) \cdot (C_3H_7NO)_{10} \cdot (H_2O)_{10}$ (IIIa). A weighed sample of complex **I** (0.97 g, 0.416 mmol) was dissolved in DMF (50 mL) on reflux. In several days, the precipitated orange crystals were filtered off and dried. The yield of complex **IIIa** was 0.71 g (46.2%). A single crystal suitable for X-ray diffraction analysis was selected from the solution. Elemental analysis was conducted for the dried crystals.

For $C_{132}H_{222}N_{20}O_{56}Si_{12}Na_6Ni_4$

Anal. calcd., % C, 42.19 H, 6.06 N, 7.58 Na, 3.73 Ni, 6.35 Si, 9.12

Found, % C, 42.17 H, 6.08 N, 7.48 Na, 3.73 Ni, 6.33 Si, 9.11

The empirical formulas of compounds **IIa** and **IIIa** derived from the elemental analysis data differ from those obtained by the X-ray diffraction analyses of the single crystals (Table 1), since a single crystal for X-ray diffraction analysis was taken from the mother liquor and elemental analysis was carried out for the dried product. This is a specific feature of all metallasiloxanes containing the solvent coordinately bound to the metal ions along with the major organometallasiloxane framework. Some solvent molecules can be removed when the sample is dried for analysis, but water molecules often occupy their sites. If poorly removable highly boiling solvent such as DMF is used as a coordinately bound solvent, its amount remained in the sample for analysis is often larger.

X-ray diffraction analyses of compounds II and III. Experimental sets of data for compounds **II** and **III** were obtained on a SMART APEX II diffractometer [43] (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode, $T = 120$ K). The structures were solved by direct methods and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for all ordered non-hydrogen atoms. A substantial disordering of atomic positions for the most part of organic fragments (phenyl substituents at the silicon atoms and DMF molecules coordinated to the sodium atom) is observed in the structure of compound **III**. In addition, the electron density peaks are localized near the Ni(1) atom in the structure of compound **III** and are modeled best of all as one DMF molecule coordinated to nickel with a population of 0.3 and two water molecules unbound to nickel with a population of 0.7. The atoms of the disordered fragments with a lower population were refined in the isotropic approximation. The hydrogen atoms of the –OH and –NH groups in the structures of compounds **II** and **III** were revealed from the difference Fourier syntheses, and the most part of them was refined in the isotropic approximation. Other hydrogen atoms in both structures were placed in the geometrically calculated positions and refined in the riding model. All calculations were performed on a personal computer using the SHELXL program package [44]. The crystallographic data and selected refinement parameters are presented in Table 1.

The full tables of coordinates of atoms, bond lengths, bond angles, and anisotropic thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1810736 (**II**) and 1810737 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown previously [26], the complex anion in compound **I** is built of two *cis*-hexaphenylcyclohexasiloxanolate ligands $[OSi(Ph)O^-]_6$ with the antiparallel arrangement. These ligands coordinate the metal matrix of four Ni^{2+} cations and four Na^+ cations by the O_M olate atoms. The cationic layer is stabilized by two μ_3-bridging ligands HO^- and by the external coordination with ten solvate *n*-butanol molecules (two *n*-butanol molecules with each sodium ion and one *n*-butanol molecule with two nickel ions). Four nickel ions are nonequivalent in pairs in such a way that two of them are completely coordinated to the oxygen atoms of the polyhedral framework and two others supplement the octahedral environment due to the coordination with the *n*-butanol molecule. The charge balance in compound **I** is achieved due to two more Na^+ cations arranged in the external sphere of the complex above the siloxane cycles and each coordinated with three *n*-butanol molecules.

Compound $Na_2(\mu\text{-}H_2O)_2(n\text{-}BuOH)_2\{[C_6H_5SiO_2]_6Ni_4Na_4(\mu_3\text{-}OH)_2[C_6H_5SiO_2]_6\} \cdot 8(n\text{-}BuOH) \cdot 2NH_3$ (**II**) is formed by the reaction of compound **I** with ammonia (Fig. 1). The phenylnickelsodium siloxane framework in compound **II** is completely retained, as well as the coordination of four sodium atoms with *n*-butanol molecules (two *n*-butanol molecules with each sodium ion). As in complex **I**, the cationic layer in compound **II** contains four Ni^{2+} cations and four Na^+ cations with two μ_3-bridging ligands $(OH)^-$. In

Table 1. Crystallographic data and refinement parameters for compounds **II** and **III**

Parameter	Value	
	II	**III**
Empirical formula	$C_{112}H_{172}N_2O_{38}Si_{12}Na_6Ni_4$	$C_{102}H_{132}N_{10}O_{36}Si_{12}Na_6Ni_4 \cdot 2.8(H_2O) \cdot 0.6(C_3H_7NO)$
FW	2864.37	2878.33
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	13.4862(12)	18.5790(7)
b, Å	16.0936(14)	18.9528(7)
c, Å	17.6206(16)	18.6702(7)
α, deg	97.569(2)	90
β, deg	108.771(2)	98.2438(9)
γ, deg	105.165(2)	90
V, Å^3	3396.0(5)	6506.3(4)
Z	1	2
ρ_{calcd}, g cm^{-3}	1.401	1.469
μ, cm^{-1}	7.47	7.83
$2\theta_{max}$, deg	60	56
Number of measured reflections	75942	97307
Number of independent reflections (R_{int})	19794 (0.0332)	15697 (0.0715)
Number of reflections with $I > 2\sigma(I)$	15298	11029
Number of refined parameters	825	918
GOOF	1.002	1.015
R_1 (for F for reflections with $I > 2\sigma(I)$)	0.0502 (15298)	0.0440 (11029)
wR_2 (for F^2 for all reflections)	0.1469	0.1189
Residual electron density (min/max), e/Å^3	−0.850/1.513	−0.698/1.088

the centrosymmetric complex anion of compound **II**, two independent nickel ions have different octahedral coordination modes. The Ni(2) ion is coordinated to four olate oxygen atoms and with oxygen atoms of two μ_3-OH groups. The Ni(1) ion is coordinated with five oxygen atoms of the polyhedral framework and the sixth position is occupied by the nitrogen atom of the coordinated ammonia molecule (Ni(1)–N(1) 2.114(2) Å). Thus, the *n*-butanol molecules coordinated to the nickel ions are substituted by ammonia molecules in compound **II**. In other respects, the structures of the polyhedral framework in compounds **I** and **II** coincide completely (Table 2), as well as the arrangement of two out-of-sphere Na^+ cations above the siloxane cycles. The Na(3)–O(2,3) distances (2.435(2) and 2.521(2) Å) coincide in fact with the Na–O(Si) distances in the polyhedral framework. However, unlike the electronic structure of compound **I**, in the crystal structure of compound **II** these Na(3) ions participate in the formation of infinite chains due to coordination with two water molecules, which serve as μ_2-bridging ligands between the adjacent complexes (Fig. 2).

Compound $\{[C_6H_5SiO_2]_6Ni_4Na_6(\mu_3\text{-}OH)_2[C_6H_5SiO_2]_6\} \cdot 4(\mu\text{-}C_3H_7NO) \cdot 6(C_3H_7NO) \cdot 2.8(H_2O) \cdot 0.6(C_3H_7NO)$ (**III**) was isolated by the crystallization of compound **I** from DMF (Fig. 3). Unlike compound **II**, in compound **III** all coordinated *n*-butanol molecules were replaced by DMF molecules bound to the sodium ions through the oxygen atom. Such a substantial change in the coor-

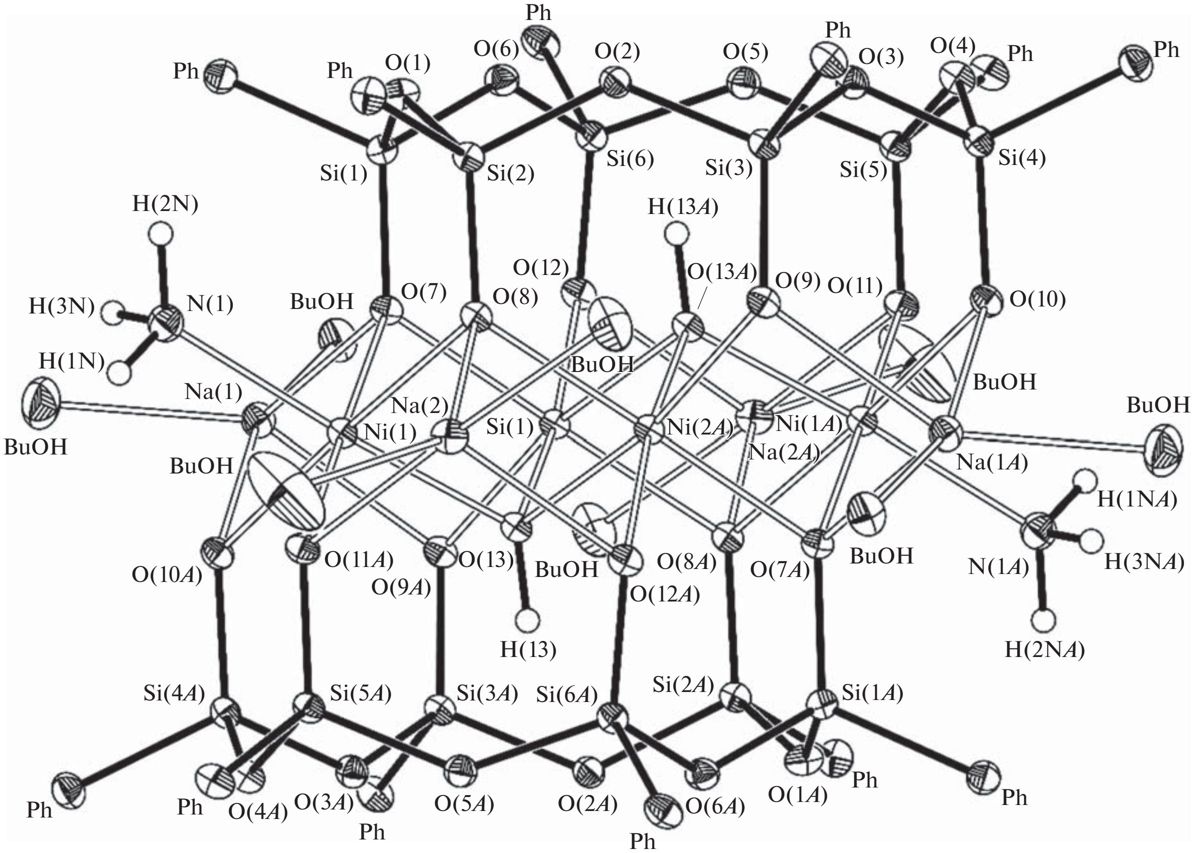

Fig. 1. Structure of the complex anion in compound **II** (only *ipso*-carbon atoms are presented for the phenyl substituents, only oxygen atoms are presented for the coordinated butanol molecules, and thermal ellipsoids are given with 30% probability).

dination environment does not lead to a significant rearrangement of the polyhedral phenylnickelsodiumsiloxane framework. The main change is related to the shift of two out-of-sphere Na^+ cations to the plane of the matrix of the metals. As a result, the layer of metal ions has the composition Ni_4Na_6, and some coordinated DMF molecules act as bridging ligands between the sodium ions. An important feature of compound **III** is a change in the coordination environment of the Ni(1) atom, which has no

Table 2. Selected bond lengths (Å) in the polyhedral frameworks of compounds **I–III**

Compound	**I** [26]	**II**	**III**
Ni–O(μ_3-OH)	2.037(7)–2.092(7)	2.051(2)–2.081(2)	2.001(2)–2.093(2)
N–O(Si)	2.060(9)–158(7)	2.072(2)–2.138(2)	2.033(2)–2.122(2)
Ni–O(BuOH)/N(NH_3)	2.142(9)	2.114(2)	
Si–O(cycle)	1.635(7)–1.658(9)	1.631(2)–1.659(2)	1.633(2)–1.644(2)
Si–O_M	1.549(9)–1.577(9)	1.576(2)–1.598(2)	1.584(2)–1.601(2)
Na–O(Si)	2.275(8)–2.485(9)	2.261(2)–2.441(2)	2.275(2)–2.337(2)
Na–O(BuOH, DMF)	2.27(1)–2.41(1)	2.292(2)–2.340(3)	2.291(3)–2.425(4)
Na(3)–O(Si)	2.50(1)–2.70(5)	2.435(2)–2.521(2)	2.270(2)–2.289(2)
Na(3)–O(BuOH, H_2O, DMF)	2.34(5)–2.79(3)	2.254(2)–2.429(3)	2.361(4)–2.395(2)

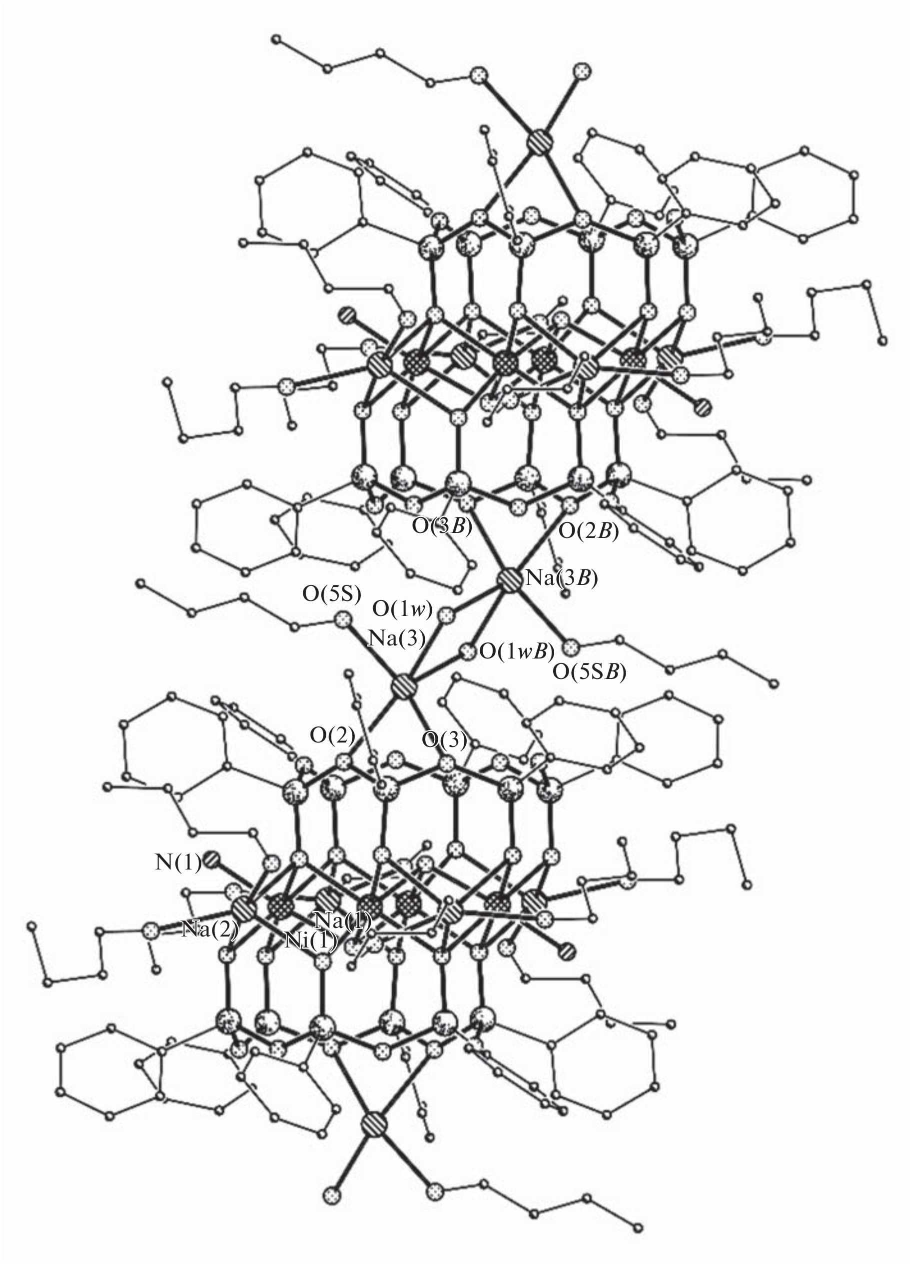

Fig. 2. Fragment of the infinite molecule in the crystal of compound **II** (hydrogen atoms are omitted).

explicitly populated site for the coordinated ligand in the octahedral environment (as the *n*-butanol molecule in compound **I** or the ammonia molecule in compound **II**). Unfortunately, an appreciable disordering of the majority of organic fragments in the structure of compound **III** does not enable us to discuss the coordination environment of the Ni(1) atom in more detail. The following data indicate in favor of the advanced assumption about the coordinately unsaturated state (tetragonal pyramid, coordination number 5) of the Ni(1) atom in compound **III**. In compound **II**, the Ni(1) atom exists in the plane of four equatorial atoms O(7), O(8), O(10*A*), and O(11*A*) (the shift of the Ni(1) atom from the mean plane of similar four oxygen atoms is 0.02 Å). At the same time, the Ni(1) atom in compound **III** is shifted by 0.14 Å from the mean plane of similar four oxygen atoms to the O(13) atom.

Thus, it is shown that the reaction of polyhedral phenylnickelsodium siloxane **I** with gaseous ammonia or its recrystallization from DMF can result in the partial or complete substitution of the outer-sphere solvate shell of *n*-butanol molecules to form new metallasiloxanes **II** and **III**. The spatially fixed rigidly high-symmetry cationic layer retains its structure in all

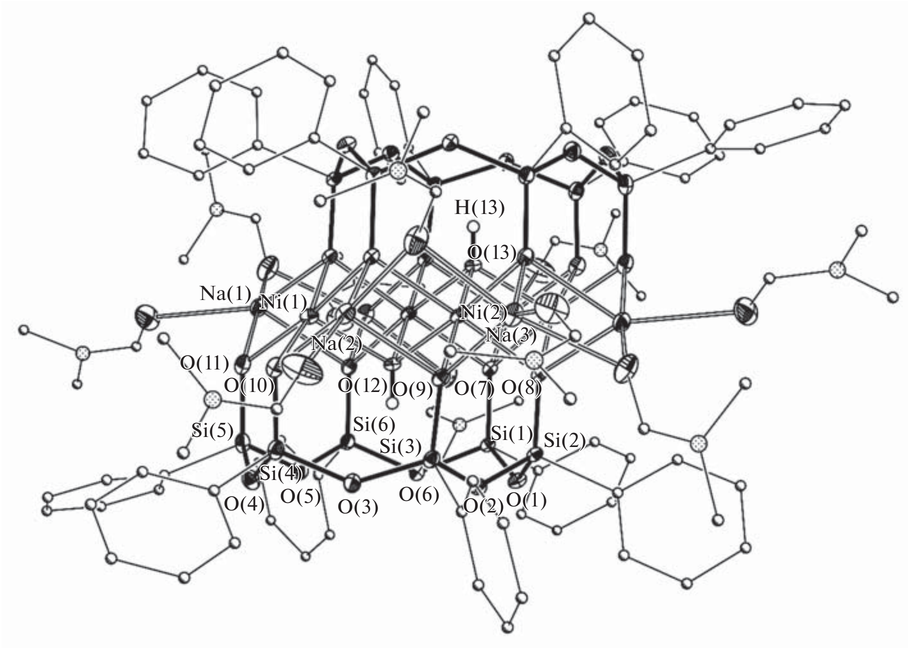

Fig. 3. Structure of compound **III** (Ni, Na, Si, and O atoms are presented by thermal ellipsoids with 30% probability, and hydrogen atoms except those of the μ_3-OH group are omitted).

compounds. The discovered coordination unsaturation of the nickel atoms in compound **III** can be significantly interesting from the viewpoint of application in catalysis.

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