New Cu$_4$Na$_4$- and Cu$_5$-Based Phenylsilsesquioxanes. Synthesis via Complexation with 1,10-Phenanthroline, Structures and High Catalytic Activity in Alkane Oxidations with Peroxides in Acetonitrile

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Received: 6 August 2019; Accepted: 17 August 2019; Published: 21 August 2019

Abstract: Self-assembly of copper(II)phenylsilsesquioxane assisted by the use of 1,10-phenanthroline (phen) results in isolation of two unusual cage-like compounds: (PhSiO$_{1.5}$)$_{12}$(CuO)$_4$(NaO$_{0.5}$)$_4$(phen)$_4$ 1 and (PhSiO$_{1.5}$)$_6$(PhSiO$_{1.5}$)$_7$(HO$_{0.5}$)$_2$(CuO)$_5$(O$_{0.25}$)$_2$(phen)$_3$. X-Ray diffraction study revealed extraordinaire molecular architectures of both products. Namely, complex 1 includes single cyclic (PhSiO$_{1.5}$)$_{12}$ silsesquioxane ligand. Four sodium ions of 1 are additionally ligated by 1,10-phenanthrolines. In turn, “sodium-less” complex 2 represents coordination of 1,10-phenanthrolines to copper ions. Two silsesquioxane ligands of 2 are: (i) noncondensed cubane of a rare Si$_6$-type and (ii) unprecedented Si$_7$-based ligand including two HOSiO$_{1.5}$ fragments. These silanol units were formed due to removal of phenyl groups from silicon atoms, observed in mild conditions. The presence of phenanthroline ligands in products 1 and 2 favored the π–π stacking interactions between neighboring cages. Noticeable that in the case of 1 all four phenanthrolines participated in such supramolecular organization, unlike to complex 2 where one of the three phenanthrolines is not “supramolecularly active”. Complexes 1 and 2 were found to be very efficient precatalysts in oxidations with hydroperoxides. A new method for the determination of the participation of hydroxyl radicals has been developed.

Keywords: alkanes; hydrogen peroxide; copper complexes; metallasilsesquioxanes

1. Introduction

Cage metallasilsesquioxanes (CLMSs) [1–9] are among objects for the study of principles of interaction of metal ion(s) and organoelement ligands. In the case of CLMSs, silsesquioxane ligands successfully play a role of structural matrix for the formation of high nuclear (e.g., Bi$_{12}$ [10],...
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Cu₉Na₆ [11,12], Cu₁₀Cs₆ [13], Fe₆Na₈ [14], Cu₁₆ [15], Mn₈Na₁₄ [16] and Cu₂₄ [17]) products. CLMSs have been thoroughly studied as active (pre)catalysts [18–24], as objects with specific magnetic (spin glass) properties [25,26] as well as pre-products for functional materials and nanoparticles [27–34]. Regarding synthetic approaches to CLMSs, three ways deserve to be mentioned as being especially effective: (i) Application of cubane Si₇ [2,4,6] or cyclic Si₄ silanols [35]; (ii) use of trisilanols [1,3,7,10,17,36,37] and (iii) self-assembly based on siloxanolate RSi(O)O⁻ units [5,8,13–16]. Recently a convenient alternative method, consisting in “dual” complexation of metal ions by siloxanolate and additional organic (P-[11], N-[12,38–40] or O-based [41]) ligands, was suggested. Taking in mind easiness (one pot implementation) of synthetic procedure, diversity of cage products (Cu₃[42], Cu₄ [11,41], Cu₅ [39], Cu₆ [42–44], Cu₉ [11,12], Cu₁₁ [38] and Co₈ [40]) and their high catalytic activity [11,12,14,39–44], we were quite interested in the further progress of this chemistry. Here we present our results devoted to the synthesis, structure elucidation and catalytic activity of new examples of cage Cu(II)silsesquioxane complexed with 1,10-phenanthroline.

2. Experimental

2.1. Synthesis

For the method of synthesis, a self-assembly reaction of [(PhSiO₁.₅)(NaO₀.₅)]ₙ as a source of silsesquioxane ligands, CuCl₂ as a source of copper ions and 1,10-phenanthroline as additional N, N-based ligand (Scheme 1) was chosen. Details of synthetic procedures are given in the ESI (Electronic Supplementary Information Table S1).

\[ \text{PhSi(OEt)}_3 + \text{NaOH} \rightarrow \text{PhSi(OEt)(OH)(ONa)} \]

1. NaOH

2. CuCl₂

3. phen

THF

DMF

\[ \text{CuCl}_2 \rightarrow \text{Cu} \]

Scheme 1. Phenanthroline-assisted self-assembly of complexes 1 and 2.

2.2. Oxidation of Alkanes and Alcohols

The oxidation reactions were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring; total volume of the reaction solution was 2.5 mL. (Caution: The combination of air or molecular oxygen and H₂O₂ with organic compounds at elevated temperatures may be explosive). Initially, a portion of 50% aqueous solution of hydrogen peroxide or 70% aqueous tert-butyl hydroperoxide was added to the solution of the catalyst and substrate in acetonitrile. The reaction solutions were analyzed by GC (Gas Chromatograph) (the instrument 3700, fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 mm × 0.3 µm; helium as a carrier gas. Attribution of peaks

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was made by comparison with chromatograms of authentic samples). Usually samples were analyzed twice, i.e., before and after the addition of the excess of solid PPh₃. This method was developed and used previously by Shul'pin [45–51]. Alkyl hydroperoxides are transformed in the GC injector into a mixture of the corresponding ketone and alcohol. Due to this we quantitatively reduced the reaction samples with PPh₃ to obtain the corresponding alcohol. This method allows us to calculate the real concentrations not only of the hydroperoxide but also of the alcohols and ketones present in the solution at a given moment.

3. Results and Discussion

3.1. Description of Compounds 1 and 2

A ratio between interacting silanolate [(PhSiO₁.₅)(NaO₀.₅)]ₓ and copper(II) chloride was oriented to let some amount of sodium ions not to be replaced by copper ions. The resulted Cu/Na mixture in the reaction system allowed us to expect a formation of an unusual cage product [11,12,38–40], instead of widespread prismatic forms of Cu-only products [15,42,52–54]. Indeed, this choice of ratio provokes the isolation of the nontrivial “double-ligated” Cu₄Na₄ product 1 (Scheme 1, Figure 1). Note, that starting silanolate units during assembly of 1 were rearranged into Si₁₂-based siloxanolate ligand of Ph₁₂Si₁₂O₁₂(OH)(O⁻)₁₁ composition, found earlier in several examples of CLMSs [55–59]. Symptomatically, that 2,2′-bipyridine containing CLMS of “Bicycle helmet” geometry, reported by some of us very recently [39], represents another type of Si₁₂-siloxanolate ligand, namely Ph₁₂Si₁₂O₁₂(OH)(O⁻)₁₁. It points out the significant flexibility of CLMSs’ self-assembly, taking in mind that both 1 and “Bicycle Helmet” [39] were isolated as THF-solvated complexes with N, N-ligands. Nevertheless, two of these products differed not only in the composition of central siloxanolate ligand but also in other features of composition. Compare, for example, (i) types of nuclearity (Cu₄Na₄ for 1 vs. Cu₅Na₁₈b), and (ii) N, N-ligand/cage’ ratio (4/1 for 1 vs. 3/1 [39]).

![Figure 1](image-url). Top left: Molecular structure of 1. Top right: Molecular structure of cage metallasilsesquioxane (CLMS) from ref. 8b. Solvating molecules of THF are not shown for clarity. Bottom left: Structure of silsesquioxane Si₁₂-ligand in 1. Bottom right: Structure of silsesquioxane Si₁₂-ligand in CLMS from ref. 8b.
Mentioned above non-rigidity of siloxanolate ligands in the procedure of CLMS' assembly found additional evidence during the study of the synthesis of Cu-silsesquioxane in dimethylformamide (DMF) media (Scheme 1, complex 2). This reaction allows unprecedented pentanuclear CLMS 2 \((\text{PhSiO}_{1.5})_6(\text{PhSiO}_{1.5})_7(\text{HO}_{0.5})_2(\text{CuO})_5(\text{O}_{0.25})_2(\text{phen})_3\) (Figure 2, top), which is very unlike pentacopper \((\text{PhSiO}_{1.5})_{10}(\text{CuO})_5\)-CLMSs, reported earlier by us [54] and the Y. Kononevich team [52]. Most likely, this difference was due to the participation of phenanthroline ligands in the reaction reporting here. Note, three phenanthroline ligands coordinated three copper ions of 2, while the remaining two copper centers were O-ligated only. This ligation was realized via participation of two types of polycyclic siloxanolate ligands. The first type represented incompletely condensed cubane silsesquioxane of \(\text{Si}_6\) composition (Figure 2, center). Unlike widespread CLMSs, obtained using \(\text{Si}_7\)-triols [2,4,6,18–20], cage metallasilsesquioxanes including \(\text{Si}_6\)-tetraol as a structural unit [60,61] are the rarest representatives of the CLMSs family. Noteworthy is that \(\text{Si}_5\)-fragment in 2 was formed in situ during the self-assembly of complex 2, while Refs. [60,61] describe the use of corresponding \(\text{Si}_6\) tetraol as a synthon. The second type of silsesquioxane skeleton in 2, to our opinion, was absolutely a unique one. First of all, this \(\text{Si}_7\)-unit (Figure 2, bottom) did not contain condensed cycles, characteristic for \(\text{Si}_7\)-triols, mentioned above [2,4,6,18–20]. Instead of that, \(\text{Si}_7\) ligand in 2 involved the \(\text{Si}_4\)-based cycle, connected to the “\(\text{Si}_3\)-based tail”. To a certain extent, this structural composition resembled the composition of the Ursa Major constellation. Secondly, this ligand contained two non-silsesquioxane fragments of the \(\text{HOSiO}_{1.5}\) composition. Taking in mind that only phenyltriethoxysilane \(\text{PhSi(OEt)}_3\) was used in the synthesis, we should witness the mild conditioned removal of organic groups from silicon (followed by the formation of silanol fragments). To the best of our knowledge, this process is a truly unprecedented one. Compare it, for example, to earlier reported process of calcination of metallasilsesquioxanes, both oligomeric [21] and cage-like ones [62–65], where cleavage of Si–R fragments required a temperature no less than 130 °C. It seems logical that mild temperature of synthesis of 2 allowed us to retain most of the phenyl groups in the silicon atoms.

![Figure 2. Cont.](image-url)
Taking into account the novelty of siloxanolate ligands obtained, chemical connectivity of copper atoms within metal-containing cluster was of interest. It was analyzed following the procedure described by Kostakis and Powell [66] to obtain the graph of the Cu-containing skeleton keeping the cluster connectivity as implemented into the ToposPro package [67]. The procedure includes analysis of metal atoms connected via bridge atoms only (here, oxygen atoms of siloxanolate anions, Figure 3). We found that metal atoms in the cages of 1 and 2 belonged to discrete clusters with, respectively, 1,2M$_4$-1, and 1,2,3M$_5$-1 topology (Figure 3). Notation of clusters is given as ND$^k_m$, where N is equal to the coordination number of topologically non-equivalent nodes, M denotes a discrete cluster (in contrast with 1-, 2- and 3-periodic architectures), $k$ is the number of metal atoms in the cluster and $m$—a classification number to distinguish topologically distinct clusters with equal ND$^k$ parameters. The majority of globular bi- and trimetallic silsesquioxanes [13,59] clusters realize the 1,2M$_4$-1 topology of the metal core, while the 1,2,3M$_5$-1 topology was not met in metallasilsesquioxanes before. Moreover, previously published databases of Co [68], Mn [69] and Ni-containing [70] high-nuclearity cluster also lack such architectures.
Both complex 1 and 2 represent specific supramolecular organization due to the $\pi-\pi$ stacking interactions of phenanthroline ligands. In the case of 1, contacts involved all four phenanthrolines leading to the formation of an extended supramolecular structure (Figure 4, top). To the best of our knowledge, analogous cases (heterometallic complexes, exhibiting packing through Na-phen units) are not widespread [71–75] and reported only for praseodymium/sodium [71], copper/sodium [72,73], iron/sodium [74], bismuth/sodium [75] and cerium/sodium [76] systems but never for CLMSs. Interestingly one of the phenanthroline ligands in the composition of complex 2 were involved in $\pi-\pi$ stacking interactions with phenyl groups of the same cage while two others provide formation of an extended structure due to contacts with phenanthrolines of neighboring cages (Figure 4, bottom).
Over the past 50 years organic chemists have invented an incredible number of synthetically useful transition metal catalyzed reaction types. In the most cases, the transition metals are complexed to sterically and electronically tunable organic ligands, which govern activity and selectivity. Such catalyst control has been made possible by combining the tools of chemistry and biology. Transition metal complexes bearing voluminous organic ligands are widely used as catalysts in various organic reactions including CH-functionalization (see reviews and original works [77–85]): “Over the past 50 years organic chemists have invented an incredible number of synthetically useful transition metal catalyzed reaction types. In the most cases, the transition metals are complexed to sterically and electronically tunable organic ligands, which govern activity and selectivity” [80]. “Capitalizing on a well-defined second coordination sphere provided by the protein around the metal cofactor, researchers have modified (artificial) metalloenzymes to react with exquisite levels of selectivity including enantio-, diastereo-, chemo-, and regioselectivity. Such catalyst control has been made possible by combining the tools of chemistry and biology” [81].

Di Stefano and co-workers [86] published a list of the following tools to distinguish between metal-based and free-radical oxidation mechanisms: (1) Alcohol/ketone ratio (A/K); (2) kinetic isotope effects (KIE); (3) reaction under argon/air; (4) the Shul’pin test for alkyl hydroperoxides; (5) regioselectivity; (6) epimerization; (7) chirality transfer; (8) labeling studies; (9) use of radical traps and (10) cyclohexene oxidation. In the present work, we applied the Shul’pin test (adding PPh₃), regioselectivity in oxidation of linear and branched alkanes as well as epimerization of 1,2-dimethylcyclohexane. Previously, we studied the catalytic systems based on the data on the selectivity of alkane oxidation and we concluded that the oxidizing species are hydroxyl radicals. The synthesized complexes have been also used in oxidation of some alcohols with tert-butyl hydroperoxide in acetonitrile.

We found that compounds 1 and 2 catalyze the oxidation of alkanes with H₂O₂ in acetonitrile. We investigated oxidations of alkanes and alcohols with hydroperoxides catalyzed by specially synthesized in this work (see above) compounds 1 and 2. The results of our investigations of some oxidation reactions catalyzed by complexes 1 and 2 under various conditions (temperatures 20–50 °C) are summarized in Figures 5–9. In some cases HNO₃ was added to the reaction solution. It could be clearly seen that after addition of PPh₃ to the reaction sample concentrations of cyclohexanone decreased while concentration of cyclohexanol after the same time period noticeably rose. This may be explained...
by the reduction of formed cyclohexyl hydroperoxide to give the corresponding alcohol (in accordance to the Shul’pin method\textsuperscript{11} (see item 4 in the list cited by Di Stefano) \cite{86}.

Figure 5. Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50\% aqueous) catalyzed by compound 1 (5 \times 10^{-4} \text{ M}) in MeCN at 50 °C. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh\textsubscript{3}. Graph A: in the absence of HNO\textsubscript{3}. Graph B: in the presence of HNO\textsubscript{3}.\textsuperscript{11}
Figure 6. Accumulation of cyclohexanol and cyclohexanone in oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50% aqueous) catalyzed by compound 2 (5 × 10^{-4} M) in MeCN at 50 °C. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh₃. Graph A: in the absence of HNO₃. Graph B: in the presence of HNO₃.
Figure 7. Accumulation of cyclohexanol and cyclohexanone in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50% aqueous) catalyzed by compound 1 (5 × 10^{-4} M) in MeCN at 50 °C. Concentrations of cyclohexanone and cyclohexanol were determined before (graph A) and after reduction of the aliquots with solid PPh\textsubscript{3} (according to the Shul'pin method [45–51]).
Figure 8. Dependence of the initial rate of oxygenate (sum cyclohexanol + cyclohexanone) formation \( W_0 \) for complex 1 on the initial concentration of cyclohexane is shown in graph A. Linearization of the curve from graph A in coordinates \( W_0^{-1} - 1/[C_6H_{12}] \) is presented in graph B. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh₃.
Figure 9. Dependence of the initial rate of oxygenate (sum cyclohexanol + cyclohexanone) formation $W_0$ for complex 2 on the initial concentration of cyclohexane is shown in graph A. Linearization of the curve from graph A in coordinates $W_0^{-1} - 1/[C_6H_{12}]$ is presented in graph B. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh$_3$.

In this work, we used a kinetic method developed by some of us [82]. To determine the kinetic characteristics of the oxidizing species generated by two catalytic systems studied in this work, the dependence of the cyclohexane oxidation rate on its initial concentration was studied (Figures 8 and 9). The nature of the dependence corresponds to the assumption of the competitive interaction of the oxidizing species X with acetonitrile (stage 1) and cyclohexane RH (stage 2):

\[ \text{H}_2\text{O}_2 + \text{catalyst} \rightarrow X \quad \text{rate of this stage is } W_i, \]  

(1)

\[ X + \text{CH}_3\text{CN} \rightarrow \ldots \rightarrow \text{products} \quad \text{rate constant } k_1, \]  

(1)

\[ X + \text{RH} \rightarrow \ldots \rightarrow \text{ROOH} \quad \text{rate constant } k_2. \]  

(2)

Here, Equation (i) is the effective reaction of generating oxidizing species X at a rate of $W_i$; Equations (1) and (2) are the transformations of CH$_3$CN and RH with the formation, in particular, various products from acetonitrile and of cyclohexyl hydroperoxide ROOH, induced by interactions that limit their rate with X. The rate constants of these interactions are $k_1$ and $k_2$, respectively. Assuming
that the concentration of species X is quasi-stationary, we obtained the following expression for the initial rate of formation of ROOH:

\[
(d[ROOH]/dt)_0 = k_2[RH]_0 W_i/(k_1[CH_3CN]_0 + k_2[RH]_0). \tag{3}
\]

Let us present Equation (3) in the form of Equation (4), convenient for the analysis of experimental data:

\[
(d[ROOH]/dt)_0^{-1} = W_i^{-1}[1 + (k_1[CH_3CN]_0/k_2[RH]_0)]. \tag{4}
\]

It follows from Figures 8B and 9B, the experimental data shown in Figures 8A and 9A, satisfy Equation (4), and this indicates the validity of the model of the competitive interaction of species X with CH₃CN and RH. Analysis of the dependence W on [CyH] for both catalysts in the frames of the model given by Equations (i)–(2) for the concurrent interaction of oxidizing species with acetonitrile and cyclohexane allowed us using Equation (4) to determine values \(k_1[CH_3CN]/k_2\): 0.44 M for 1 and 0.66 M for 2. These parameters were sufficiently higher than characteristics known for the reactions of cyclohexane with hydroxyl radicals: Interval 0.04–0.1 M. It is important to emphasize here that the regioselectivity parameters collected in Table 1 indicated that oxidizing species in the cases of both catalysts 1 and 2. The contradiction between conclusions made on the basis of the kinetic study and investigation using selectivity parameters can be understood if we assumed that the approach of reaction centre to acetonitrile and cyclohexane molecules was different due to their different special characteristics. Concentrations of CH₃CN and CyH close to the reaction center and in solution bulk volume were different. Due to this the constant ratios \(k_1/k_2\) in the reactions catalyzed by 1 or 2 differ from that found for the interactions with the participation of free hydroxyl radicals.

| Entry | Catalytic System | C(1):C(2):C(3):C(4) | \(1^\text{cise}-2^\text{cis}-3^\text{cis}\) | \(\text{trans}/\text{cis}\) |
|-------|----------------|---------------------|-----------------|-------------------|
| 1     | Catalyst 1     | 1.0:5.9:6.2:5.6     | 1.0:5.6:14.0    | 0.8               |
| 2     | Catalyst 1 + HNO₃ | 1.0:4.5:4.3:3.9      | 1.0:4.7:11.3 | 0.8               |
| 3     | Catalyst 2     | 1.0:5.3:5.3:5.4     | 1.0:6.2:17.4    | 0.9               |
| 4     | Catalyst 2 + HNO₃ | 1.0:5.7:5.7:5.2      | 1.0:5.4:15.0 | 0.75              |
| 5     | VO₃⁻/PCA b     | 1.0:6.0:7.0:5.0   | 1.9:37          |                   |
| 6     | \([\text{Mn}_2\text{O}_2(\text{O})_2]_2^+/\text{MeCO}_2\text{H}^c\) | 1:46:35:34 | 1:26:200 |                   |

Parameter C(1):C(2):C(3):C(4) is the relative normalized (calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and of the chain of \(n\)-heptane. Parameter \(1^\text{cise}-2^\text{cis}-3^\text{cis}\) is the relative normalized reactivities of hydrogen atoms at the primary, secondary and tertiary carbons of methylcyclohexane and isooctane. Parameter \(\text{trans}/\text{cis}\) is the ratio of isomers of tert-alcohols with mutual \(\text{trans}\) and \(\text{cis}\)-orientation of the methyl groups formed in the oxidation of \(\text{cis}\) and \(\text{trans}\)-1,2-dimethylocyclohexane. All parameters were measured after the reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. b PCA is pyrazine-2-carboxylic acid. For this system, see Ref. [83]. c \(L\) is trimethyltriazacyclononane. For this system, see Ref. [84].

As shown above, the low selectivity of the oxidative effect of X species, which is close to the selectivity found for reactions involving hydroxyl radicals, and this indicates that hydroxyl radicals are generated in the catalytic systems studied in the present work. Similar results (a decrease in the relative reactivity of the oxidizing species for cyclohexane in comparison with acetonitrile) were obtained earlier by us in clarifying the nature of the oxidizing species during the catalysis of the decomposition of hydrogen peroxide on the complex palanquin-like Cu₄Na₄ silsesquioxane [41] as well as using aluminum nitrate [85].

We found that the additives of HNO₃ reduced the catalytic activity of both the 1 complex and the 2 complex (see Figures 8A and 9B). This difference could be explained either by a change in the structure of the initial complex 1 or 2 in a solution containing HNO₃, or by a change in the rate of interaction of complexes 1 and 2 with H₂O₂. The acid probably broke up the initial complex into many smaller particles, which were less active in catalysis. The data on the oxidation of linear \(n\)-heptane
(see Table 1) showed that the oxidative effect of the species generated by the catalytic decomposition of H₂O₂ in the presence of compounds 1 or 2, both in the absence of HNO₃ and in its presence, was close to the regioselectivity characteristic of the reaction with hydroxyl radical. On the other hand, analysis of the dependence of the initial oxidation rate of cyclohexane on its initial concentration during catalysis of the H₂O₂ decomposition on complex 1 in the presence of HNO₃ in the frames of a homogeneous model (i)–(2) of the competitive interaction of the oxidizing species with cyclohexane and acetonitrile (similar to the one given above for the reaction in the absence of HNO₃) showed that the reactivity of the oxidizing particle corresponded to the participation of the hydroxyl radical: The value of $k_1[\text{CH}_3\text{CN}]/k_2 = 0.11$ M was close to the values typical for the hydroxyl radical parameters 0.04–0.1 M. While for complex 1 in the absence of HNO₃, the value of $k_1[\text{CH}_3\text{CN}]/k_2 = 0.44$ M differed significantly from that which were typical for reactions involving hydroxyl radicals.

The combination of our results shows that in the presence of nitric acid the structure of the initial complex was likely changed, namely the complex structures of multicore complexes were transformed into simpler compounds, the reaction centers of which were equally accessible to both acetonitrile and cyclohexane. This led to a difference in the reactivity of complexes 1 and 2 in the presence of HNO₃ from that in its absence (when the reaction centers were more accessible for interaction with acetonitrile than with cyclohexane).

The complexes 1 and 2 were also used in the oxidation of some alcohols with tert-butyl hydroperoxide in acetonitrile. 1-Phenylethanol could be transformed into acetophenone in almost the quantitative yield (Figures 10 and 11). Cyclohexanol and heptanol-2 were oxidized to the corresponding ketones less efficiently.

![Figure 10. Accumulation of cyclohexanone (curve 1), and acetophenone (curve 2) in the oxidation of cyclohexanol (0.5 M) or 1-phenylethanol (0.5 M), respectively, with tert-butyl hydroperoxide (1.5 M) catalyzed by complex 1 (5 × 10⁻⁴ M) at 50 °C in acetonitrile. In order to quench the oxidation process concentrations of products were measured by GC only after the reduction of the reaction sample with solid PPh₃.](image-url)
We presented here non-trivial Cu₄Na₄ 1 and Cu₅ 2 phenylsilsesquioxanes as complexes with 1,10-phenanthroline ligands. The cage structure of complex 1 was characterized by the presence of the Si₁₂-based ligand, favoring the contacts of external sodium ions to phenanthroline molecules. Complex 2 involved two different types of silsesquioxane fragments, namely the Si₆-non-condensed cubane and Si₇-“Ursa Major” ligand. The latter represents a very unusual removal of phenyl groups from silicon atoms with simultaneous formation of Si–OH groups. It points to a complicated way of self-assembly of metallasilsesquioxane cages especially in the presence of additional organic ligands. Stacking interactions of phenanthrolines formed extended supramolecular assembly of both compounds 1 and 2 in crystal packing. Catalytic tests of 1 and 2 showed their high activity in oxidations of alkanes and alcohols with peroxides. Further investigation of the “sesquioxane O-ligand plus N,N-ligand” approach to isolation of catalytically prospective Cu(II)-based structures is currently on way in our team. A new method for the determination of the participation of hydroxyl radicals was developed.

4. Conclusions

Figure 11. Accumulation of cyclohexanone (curve 1) and acetoephone (curve 2) in the oxidation of cyclohexanol (0.5 M) or 1-phenylethanol (0.5 M), respectively, with tert-butyl hydroperoxide (1.5 M) catalyzed by complex 2 (5 × 10⁻⁴ M) at 50 °C in acetonitrile. In order to quench the oxidation process concentrations of products were measured by GC only after the reduction of the reaction sample with solid PPh₃.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/9/701/s1, Table S1. Crystallographic data for 1–2.

Author Contributions: A.N.B. and G.B.S. conceived and designed the experiments; G.S.A., N.S.I., P.V.D. and L.S.S. performed the experiments; A.N.B., E.S.S., M.M.L., Y.N.K., A.A.K. and G.B.S. analyzed the data; A.N.B. and G.B.S. wrote the paper.

Funding: This research was funded by the RUDN University Program “5-100”, the Russian Foundation for Basic Research (Grant Nos. 19-03-142, 17-03-00993), the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007), as well as by the Initiative Program in the frames of the State Task 0082-2014-0007, “Fundamental regularities of heterogeneous and homogeneous catalysis.”

Acknowledgments: The publication has been prepared with the support of the «RUDN University Program 5-100» and funded by RFBR according to Research Projects Grant Nos. 17-03-00993, 19-03-00142, 19-03-00488, 16-29-05180, the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007), as well as by the Initiative Program in the frames of the State Tasks 0082-2014-0004 and 0082-2014-0007 “Fundamental regularities of heterogeneous and homogeneous catalysis”. Elemental analysis was performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS. This work was also performed within the framework of the Program of Fundamental Research of the Russian Academy of Sciences for 1013-2020 on the research issue of IChP RAS No. 47.16. State registration number of Center of Information Technologies and Systems for Executive Power Authorities (CITTIS).
Conflicts of Interest: The authors declare no conflict of interest.

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