



**HAL**  
open science

## High-Cluster (Cu 9 ) Cage Silsesquioxanes: Synthesis, Structure, and Catalytic Activity

Grigorii S Astakhov, Alexey N Bilyachenko, Alexander A Korlyukov, Mikhail M Levitsky, Lidia S Shul'pina, Xavier Bantreil, Frédéric Lamaty, Anna V Vologzhanina, Elena V Shubina, Pavel V. Dorovatovskii, et al.

► **To cite this version:**

Grigorii S Astakhov, Alexey N Bilyachenko, Alexander A Korlyukov, Mikhail M Levitsky, Lidia S Shul'pina, et al.. High-Cluster (Cu 9 ) Cage Silsesquioxanes: Synthesis, Structure, and Catalytic Activity. *Inorganic Chemistry*, 2018, 57 (18), pp.11524-11529. 10.1021/acs.inorgchem.8b01496 . hal-02370758

**HAL Id: hal-02370758**

**<https://hal.science/hal-02370758v1>**

Submitted on 5 Feb 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# High-Cluster ( $\text{Cu}_9$ ) Cage Silsesquioxanes: Synthesis, Structure, and Catalytic Activity

Grigorii S. Astakhov,<sup>†,‡</sup> Alexey N. Bilyachenko,<sup>\*,†,‡,§</sup> Alexander A. Korlyukov,<sup>†,§</sup> Mikhail M. Levitsky,<sup>†</sup> Lidia S. Shul'pina,<sup>†</sup> Xavier Bantreil,<sup>||</sup> Frédéric Lamaty,<sup>\*,||</sup> Anna V. Vologzhanina,<sup>†</sup> Elena S. Shubina,<sup>†</sup> Pavel V. Dorovatovskii,<sup>⊥</sup> Dmytro S. Nesterov,<sup>#</sup> Armando J. L. Pombeiro,<sup>#</sup> and Georgiy B. Shul'pin<sup>\*,||,∇</sup>

<sup>†</sup>Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Strasse 28, Moscow, Russia

<sup>‡</sup>Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklay Strasse 6, Moscow, Russia

<sup>§</sup>Pirogov Russian National Research Medical University, Ostrovitianov Strasse 1, Moscow, Russia

<sup>||</sup>Institut des Biomolécules Max Mousseron, UMR 5247, CNRS, Université de Montpellier, ENSCM, Site Triolet, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

<sup>⊥</sup>National Research Center "Kurchatov Institute", Akademika Kurchatova Place 1, Moscow, Russia

<sup>#</sup>Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>∇</sup>Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, 119991 Moscow, Russia

<sup>∇</sup>Plekhanov Russian University of Economics, Stremyannyi Pereulok, dom 36, 117997 Moscow, Russia

**ABSTRACT:** Unusual high-cluster ( $\text{Cu}_9$ ) cage phenylsilsesquioxanes were obtained via complexation of in situ  $\text{Cu}^{\text{II}}$ , Na-silsesquioxane species formed with phenanthroline and neocuproine. In the first case, phenanthroline, acting as “a silent ligand” (not participating in the composition of the final product), favors the formation of an unprecedented cagelike phenylsilsesquioxane of  $\text{Cu}_9\text{Na}_6$  nuclearity, **1**. In the second case, neocuproine ligands withdraws two Cu ions from the metallasilsesquioxane matrix, producing two cationic fragments  $\text{Cu}^+(\text{neocuproine})_2$ . The remaining metallasilsesquioxane is rearranged into an anionic cage of  $\text{Cu}_9\text{Na}_4$  nuclearity, finalizing the formation of a specific ionic complex, **2**. The impressive molecular architecture of both types of complexes, e.g., the presence of different (cyclic/acyclic) types of silsesquioxane ligands, was established by single-crystal X-ray diffraction studies. Compound **1** was revealed to be highly active in the oxidative amidation of benzylic alcohol and the catalyst loading could be reduced down to 100 ppm of Cu. Catalytic studies of compound **1** demonstrated its high activity in hydroperoxidation of alkanes with  $\text{H}_2\text{O}_2$  and oxidation of alcohols to ketones with *tert*-BuOOH.

## INTRODUCTION

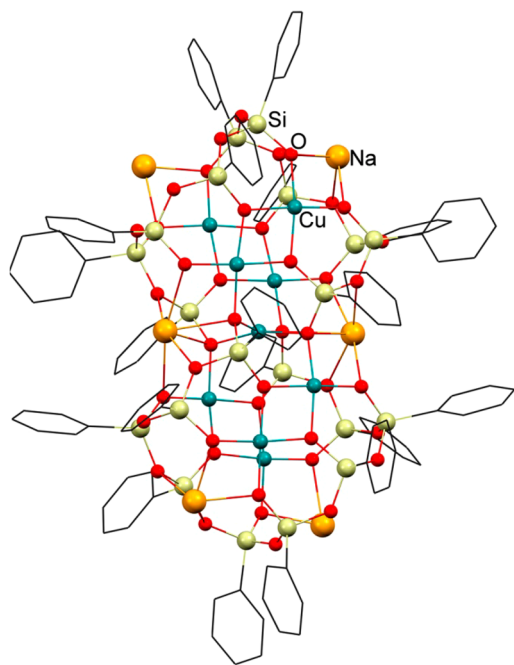
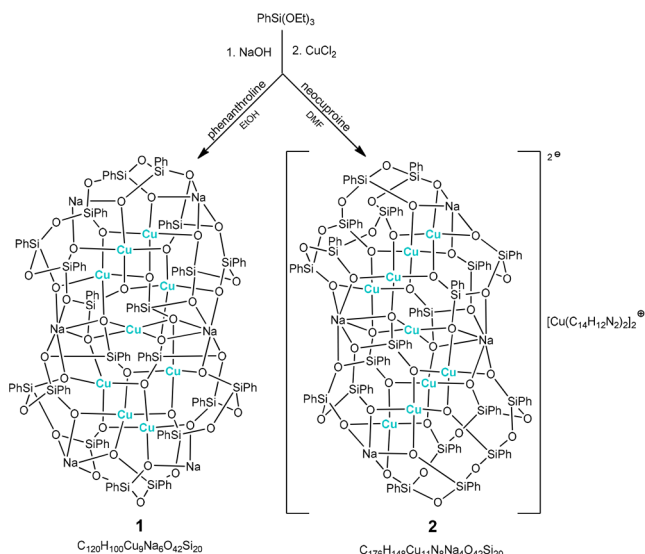
Hybrid inorganic–organic molecular materials are the focus of both academia and industry chemists because of their unusual reactivity, structure formation principles, and numerous potential applications.<sup>1</sup> Among the best models for such hybrid materials are derivatives of siloxanes and molecular combinations of inorganic (Si–O–Si) skeletons and organic (R–Si) surroundings.<sup>2</sup> An exclusive feature of monosubstituted siloxanes (silsesquioxanes of the general formula  $[\text{RSiO}_{1.5}]_n$ ) is an ability to form different polyhedral clusters.<sup>3</sup> These well-defined polyhedral structures are the objects of utmost interest as precursors of materials in high demand.<sup>4</sup> In turn, it should be mentioned that silsesquioxanes are suitable

matrixes for the production of cagelike metal-containing derivatives.<sup>5</sup> Important data concerning the reactivity and structure formation were reported for the cases when additional ligands (e.g., 1,2,3,4,5-pentamethylcyclopentadiene,<sup>6</sup> silylamido,<sup>7</sup> and triethylamine<sup>8</sup>) were used along with the silsesquioxane one in the assembly of polyhedral metal-lacompleses. In all of these works, the “ligands-synergy” principle was reported when two types of ligands (silsesquioxane and organic ones) coordinated metal ions of the cagelike product.

## RESULTS AND DISCUSSION

Here we discuss a different scenario of additional ligand involvement in the cage metallasilsesquioxane synthesis. First, the self-assembly reaction of the in situ formed sodium phenylsiloxanolate  $[(\text{PhSiO}_{1.5})(\text{NaO}_{0.5})]_n$  and copper(II) chloride in the presence of 1,10-phenanthroline (ethanol media) gave unprecedented cage-like  $\text{Cu}_9\text{Na}_6$ -silsesquioxane **1** (Scheme 1 and Figure 1, top).

Scheme 1. Reaction Scheme of the Synthesis of **1** and **2**



It is worth mentioning that the phenanthroline ligand is not participating in the composition of the final product; nevertheless, its influence on the reaction course could not be denied: early reported “phenanthroline-less” synthesis of  $\text{Cu}_2\text{Na}_2$ -phenylsilsesquioxane in ethanol media gave a  $\text{Cu}_2\text{Na}_2$  complex<sup>9</sup> of principally different molecular topology. Thus, it may be concluded that phenanthroline acts as a “silent witness” ligand, and this effect was found to be reproducible (additional

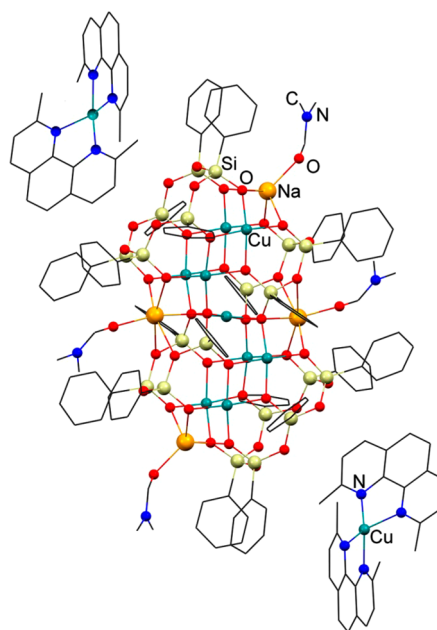
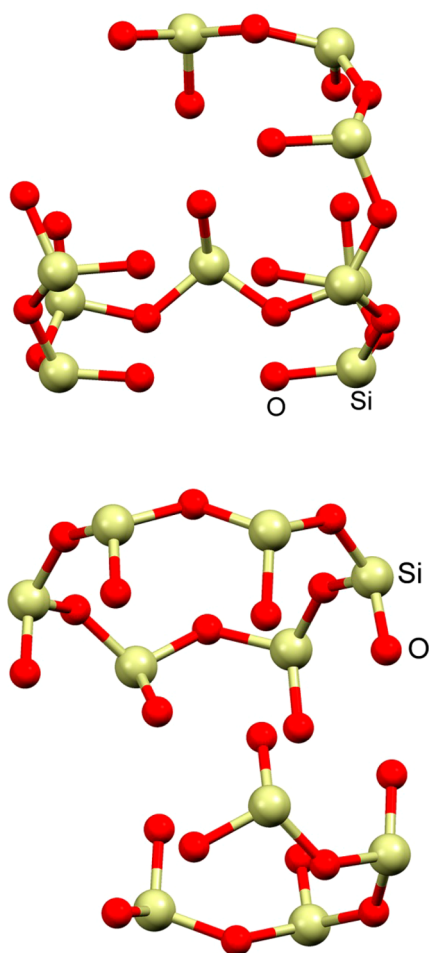


Figure 1. Molecular structures of **1** (top) and **2** (bottom). Solvating ethanol and water molecules of **1** are omitted for clarity. Color code: Si, yellow; O, red; Cu, green; N, blue; C, black.

runs of this reaction gave an analogue of complex **1**, with small differences from **1**; see complex **1a**; Figures S1 and S2).

In the second stage of work, a similar synthetic procedure but in the presence of another type of N-based ligand, neocuproine, was studied. To our surprise, this reaction provoked the formation of a principally different type of molecular architecture, compound **2** (Scheme 1 and Figure 1, bottom). To the best of our knowledge, compound **2** represented a novel principle of metal-containing cage compound design in conditions of the presence of O and N ligands in the reaction mixture. The only example of similar reaction in the presence of P-ligand was presented by some of us in recent work.<sup>5g</sup> The product **2** composition could be described as a consequence of unusual Cu ion redistribution between two types of ligands. Namely, neocuproine ligands form two cationic fragments  $\text{Cu}^+(\text{neocuproine})_2$ , while  $\text{Cu}_9\text{Na}_4$ -silsesquioxane plays the role of a negatively ( $2-$ ) charged component of compound **2**. Such a difference of behavior between phenanthroline and neocuproine could be explained by the better  $\sigma$  donation of the latter ligand, as demonstrated in the formation of copper ethylene complexes.<sup>10</sup>

The compositions of the silsesquioxane fragments of complexes **1** and **2** are quite different from each other. Namely, compound **1** comprises two acyclic  $\text{Ph}_{10}\text{Si}_{10}\text{O}_{21}$  ligands, unprecedented for cage metallasilsesquioxanes (Figure 2, top). In turn, the cage component of complex **2** includes two pairs of ligands: cyclic  $(\text{PhSiO}_{1.5})_6$  and acyclic  $(\text{PhSiO}_{1.5})_4$  (Figure 2, bottom). While  $(\text{PhSiO}_{1.5})_6$  ligands are widespread among metallasilsesquioxane structures,<sup>5a,b</sup> we could cite the only work-described  $(\text{PhSiO}_{1.5})_4$  ligands in the composition of cage Ti-silsesquioxanes.<sup>11</sup> This publication, unlike compound **2**, reported cyclic  $(\text{PhSiO}_{1.5})_4$  rings, sandwiched between Ti-based planes. Detailed topological analysis of the structures of compounds **1** and **2** is presented in Figure S4. Finally, we could mention Mn-based phenylsilsesquioxane<sup>12</sup> possessing the same  $[(\text{PhSiO}_{1.5})_6$  and  $(\text{PhSiO}_{1.5})_4]$  combination of ligands



**Figure 2.** Silsesquioxane ligand structures in **1** (top) and **2** (bottom).

as compound **2**. It is worth noting that the resulting structure of the compound from ref **12** is quite unlike complex **2**.

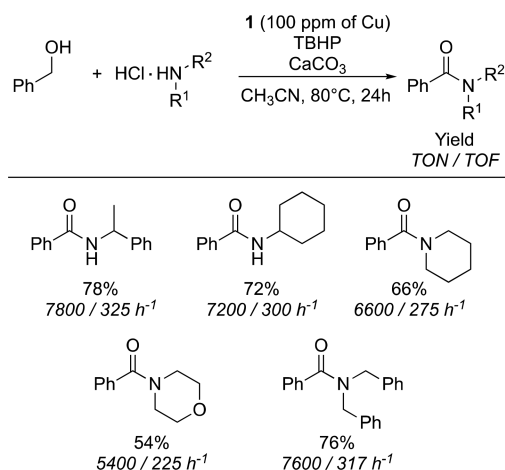
The structure and composition of Si–O–Si skeletons in both products **1** and **2** are worth mentioning as new evidence of the role of additional factors during Si–O–Si fragment assembly. It is known that the basic reaction  $[\text{PhSi}(\text{OR}')_3 \text{ with NaOH}]$  leads to the cyclic trimer or tetramer product  $[\text{PhSi}(\text{O})\text{ONa}]_n$ ,  $n = 3$  or  $4$ ; **Figure S3**.<sup>5a,13</sup> In turn, numerous further syntheses, using these trimers or tetramers for interaction with transition-metal salts, showed the structural rearrangement of these cycles into ligands of other forms.<sup>5a,14</sup> Keeping in mind that the procedures presented here that allowed the isolation of compounds **1** and **2** are even more complicated because of the involvement of additional N ligands, it is not surprising that the silsesquioxane ligand topology in **1** and **2** is far from the classical one.

Regarding the properties of complexes **1** and **2**, we could state that both compounds are air-stable, nonhygroscopic, and well soluble in polar organic solvents (e.g., *N,N*-dimethylformide, dimethyl sulfoxide, or benzonitrile) or in their mixtures with aromatic solvents (benzene and toluene).

We previously reported the activity of cage-like metal-silsesquioxanes (CLMSs) as precatalysts in the homogeneous catalysis of highly relevant organic reactions: amidation and hydrocarbons functionalization.<sup>15</sup> Importantly, the use of CLMSs allowed minimization of the catalyst loading (down to 100 ppm of Cu) with retention of the catalytic activity. A

quick optimization of the reaction conditions, for the formation of amides directly from alcohol,<sup>16</sup> revealed that compound **1** was as efficient as the previously reported CLMSs because only 100 ppm of Cu was required to catalyze the reaction. When benzyl alcohol was reacted with different amines, protected as their ammonium salt, in the presence of calcium carbonate, *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant, and **1** as the catalyst, the corresponding amides could be isolated in good yield (**Scheme 2**). To ensure

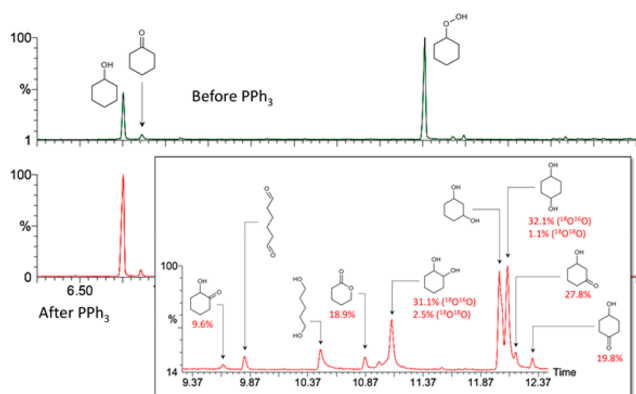
**Scheme 2.** Catalytic Activity of Compound **1** in Oxidative Amidation<sup>a</sup>



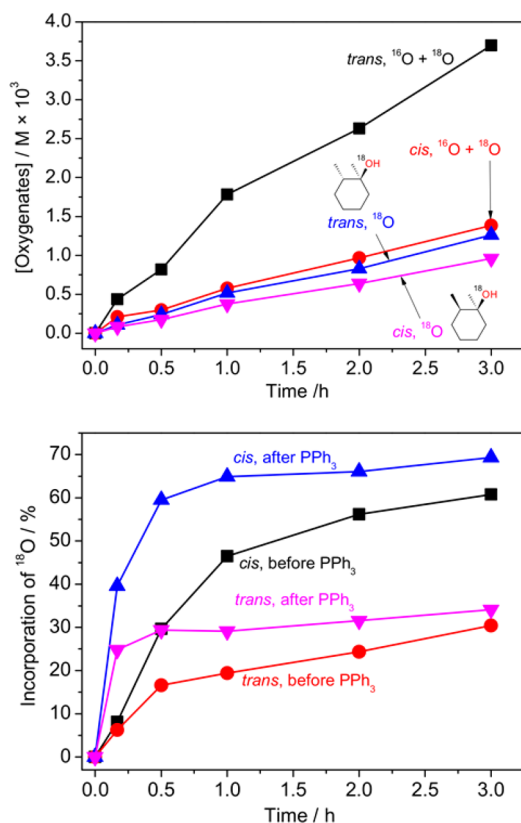
<sup>a</sup>Reaction conditions: ammonium chloride (0.5 mmol), benzyl alcohol (1.0 mmol),  $\text{CaCO}_3$  (0.25 mmol), TBHP (5.5 M, 2.5 mmol), **1** (0.01 mol % of Cu),  $\text{CH}_3\text{CN}$  (1 mL), 80 °C, 24 h.

that compound **1**, and not traces of metals, was indeed responsible for the catalytic activity, high-purity calcium carbonate (>99.999% purity) was used. Because low catalyst loading was used, the turnover number and frequency (TON and TOF) were calculated.<sup>17</sup> The reaction was found to be efficient with primary and secondary amines, with TON and TOF values reaching 7700 and 325 h<sup>-1</sup>, respectively. These values are slightly lower than those obtained with a Cu<sub>4</sub>-CLMS featuring a globulelike structure (TON and TOF of 9400 and 392 h<sup>-1</sup>, respectively).<sup>15</sup> However, compound **1** was undoubtedly more efficient than the CuO that was used in our seminal publication on this reaction, with TON and TOF values of 44 and 11 h<sup>-1</sup>, respectively.<sup>16e</sup>

Impressive results were obtained in the catalyzed alkane oxidations with peroxides ( $\text{H}_2\text{O}_2$  and *m*-chloroperoxybenzoic acid). Oxidation of cyclohexane (CyH) with  $\text{H}_2\text{O}_2$ , in the presence of **1** as a catalyst and  $\text{HNO}_3$  as a promoter either in air (see **Figures S10–S15**) or under an atmosphere of <sup>18</sup>O<sub>2</sub> (see **Figures 3** and **4** and **S16–S24**), afforded cyclohexyl hydroperoxide as the main reaction product, which is selectively reduced with  $\text{PPh}_3$  (refs **18**) to produce cyclohexanol. The highest incorporation of <sup>18</sup>O into cyclohexyl hydroperoxide was observed at the beginning of the reaction (**Figure S16**). The chromatogram recorded before the addition of  $\text{PPh}_3$  reveals a strong peak of cyclohexyl hydroperoxide, disappearing upon treatment. The pattern of byproducts (**Figure 3**) is typical for reaction systems oxidizing with hydroxyl radicals, showing isomers of cyclohexanediols and hydroxycyclohexanones. Cyclohexanediols are mainly single <sup>18</sup>O-labeled. Hydroxycyclohexanones are probably only labeled



**Figure 3.** Fragments of the chromatograms showing the main reaction products and byproducts (inset) in the course of CyH oxidation with  $\text{H}_2\text{O}_2$ , in the presence of  $\text{HNO}_3$ , catalyzed by **1** (for conditions, see Figure S16), before (top, green) and after (bottom, red) the addition of solid  $\text{PPh}_3$  to the reaction sample. Percentages indicate the incorporations of  $^{18}\text{O}$  into the respective oxygenates measured after the addition of  $\text{PPh}_3$ . The incorporation of  $^{18}\text{O}$  into the main products is shown in Figure S16, right.



**Figure 4.** Top: Accumulations of all and  $^{18}\text{O}$ -labeled trans and cis tertiary alcohols in the course of oxidation of *cis*-1,2-dimethylcyclohexane (0.14 M) with *m*-CPBA (0.18 M), in the presence of  $\text{HNO}_3$  (0.05 M), catalyzed by **1** ( $5 \times 10^{-4}$  M), in  $\text{CH}_3\text{CN}$  at  $50^\circ\text{C}$ ; measured after the addition of solid  $\text{PPh}_3$  to the samples. Bottom: Dependence of the  $^{18}\text{O}$  percentage in the tertiary alcohols.

at the hydroxyl O atom because of oxygen exchange of their ketone groups with  $\text{H}_2^{16}\text{O}$ .

We clearly realize that synthesized complexes are only precatalysts in hydrocarbon oxidations. Under the action of  $\text{HNO}_3$  acid, the complex is modified to open fragments, with

reaction centers available for approaching both  $\text{H}_2\text{O}_2$  and the substrate. As in the case of oxidations catalyzed by polyoxometallates, in our oxidation, a few species with active reaction centers work. Figures S10–S14 demonstrate peculiarities of CyH oxidation with  $\text{H}_2\text{O}_2$  in acetonitrile. The maximum yield of the products was 21%. The products of methylcyclohexane oxidation by the same system are shown in Figure S15. Oxidations of *n*-heptane and *n*-octane allowed us to measure regioselectivity parameters: 1:5.4:5.4:4.9 and 1:5.4:5.3:4.8, respectively. The reaction of *cis*-1,2-dimethylcyclohexane with  $\text{H}_2\text{O}_2$  catalyzed by compound **1** gave a trans/cis ratio of 1.0 for *tert*-alcohols. The interaction of *tert*-butyl hydroperoxide (1.5 M) with 1-phenylethanol or cyclohexanol (0.5 M) in the absence of  $\text{HNO}_3$  afforded after 10 or 5 h at  $60^\circ\text{C}$  cyclohexanone or acetophenone in 63% or 98% yield, respectively.

The system **1**/ $\text{HNO}_3$ / $\text{H}_2\text{O}_2$  shows low stereoselectivity with 14% retention of the stereoconfiguration (RC), corresponding to a trans/cis ratio of 1.34 of tertiary alcohols. Such a value of the RC index indicates the involvement of free alkyl radical intermediates. The normalized bond selectivity for *cis*-1,2-dimethylcyclohexane is  $3^\circ:2^\circ:1^\circ = 90:21:1$ . Although the ratio  $3^\circ:2^\circ = 4.3:1$  is expected for the hydroxyl radical range,<sup>19</sup> the amounts of primary oxygenates are abnormally low. This may be explained by a high reactivity of closely located tertiary H atoms of *cis*-1,2-dimethylcyclohexane.

Oxidation of *cis*-1,2-dimethylcyclohexane with *m*-CPBA, catalyzed by **1**, in the presence of a  $\text{HNO}_3$  promoter and under an atmosphere of  $^{18}\text{O}_2$ , afforded much higher stereoselectivity with an RC index of up to 51% (trans/cis ratio of up to 3.1 of tertiary alcohols). The incorporation of  $^{18}\text{O}$  into the tertiary alcohols is also higher than those in the case of  $\text{H}_2\text{O}_2$ , reaching 70% after 3 h (Figure 4, bottom). Remarkably, while *cis*-alcohol accumulated ca. 2 times more  $^{18}\text{O}$  than *trans*-alcohol (in percent), the absolute amounts of both  $^{18}\text{O}$ -labeled alcohols are nearly equal (Figure 4, top). The initial reaction rates of  $^{18}\text{O}$ -labeled tertiary alcohols ( $1.4 \times 10^{-7}$  and  $1.0 \times 10^{-7}$   $\text{M s}^{-1}$  for *trans*- and *cis*-alcohols, respectively) are ca. 2 times lower than the overall initial rates ( $5.0 \times 10^{-7}$  and  $1.7 \times 10^{-7}$   $\text{M s}^{-1}$  for *trans*- and *cis*-alcohols, respectively).

Recently, we found that a hexacopper complex with neocuproine (an analogue of complex **2**) is a highly efficient homogeneous catalyst in the oxidation of alkanes and alcohols with peroxides.<sup>20</sup> All of the peculiarities of alkane oxidation indicate that the oxidation with  $\text{H}_2\text{O}_2$  occurs with the participation of free hydroxyl radicals. The hexacopper complex with neocuproine also efficiently catalyzes the oxidation of alcohols to ketones with TBHP in acetonitrile. The oxidation of alcohols apparently involves the generation of hydroxyl radicals.

## CONCLUSIONS

In summary, two unique cage Cu,Na-silsesquioxanes were synthesized through self-assembly reactions of sodium siloxanolate species with  $\text{CuCl}_2$ . The specific role of N-based ligands (phenanthroline and neocuproine) in this reaction was demonstrated. Namely, the presence of phenanthroline provokes the formation of compound **1**, containing no phenanthroline moieties in the composition (phenanthroline as a “silent witness”<sup>21</sup> ligand). In turn, neocuproine-assisted synthesis led to the formation of complex **2** with an unusual redistribution of Cu centers between O (silsesquioxane) and N (neocuproine) ligands. These observations point to the huge

influence of various types of ligands, depending on their binding affinity, on the mechanism of cage metallacomplex formation. It is worth noting that small differences in the N-ligand structures (phenanthroline vs neocuproine) cause the formation of dramatically different cage products. This indicates that the formation of cage metallasilsesquioxane is complicated, especially in the presence of additional ligands, which could provoke “ligand-to-metal” competitions and metal redistribution. In turn, the isolation of compounds **1** and **2** was performed for the conditions of different solvent media. No doubt, the difference in the solvates’ surroundings may also be crucial during the assembly/crystallization of the cage product. In summary, we could state that at least three parameters could influence/control the metallasilsesquioxane formation: (i) ratio between “key elements” in reaction media, namely, Si:Cu:Na:N; (ii) nature of the ligand; (iii) ability of solvent molecules to play a role of solvating ligands. All of these factors could be of high influence for the process under discussion, and in our future reports, we will try to shed some light on this point. Compound **1** was found to be efficient in the alkane oxidation and oxidative amidation of benzylic alcohols, with a catalyst loading down to 100 ppm of Cu and TON and TOF values of up to 7800 and 325 h<sup>-1</sup>. Compound **1** exhibited high activity in the hydroperoxidation of alkanes with H<sub>2</sub>O<sub>2</sub>.

#### Accession Codes

CCDC 1834447–1834449 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

##### Corresponding Authors

\*E-mail: [bilyachenko@ineos.ac.ru](mailto:bilyachenko@ineos.ac.ru).

\*E-mail: [frederic.lamaty@umontpellier.fr](mailto:frederic.lamaty@umontpellier.fr).

\*E-mail: [shulpin@chph.ras.ru](mailto:shulpin@chph.ras.ru).

##### ORCID

Alexey N. Bilyachenko: 0000-0003-3136-3675

Xavier Bantreil: 0000-0002-2676-6851

Anna V. Vologzhanina: 0000-0002-6228-303X

Elena S. Shubina: 0000-0001-8057-3703

Pavel V. Dorovatovskii: 0000-0002-2978-3614

Georgiy B. Shul'pin: 0000-0002-7053-4812

##### Author Contributions

The manuscript was written through contributions of all authors.

##### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The publication was prepared with the support of RUDN University Program 5-100 and funded by RFBR according to Research Projects 16-03-00254, 16-53-150008, 16-29-05180,

and 17-03-00993, French Embassy in Moscow, University of Montpellier, CNRS (Programme de Recherche Conjoint). Synchrotron single-crystal diffraction measurements were performed at the unique scientific facility Kurchatov Synchrotron Radiation Source supported by the Ministry of Education and Science of the Russian Federation (Project code RFMEFI61917X0007). This work was also supported by the State within the frameworks of the state task for ICP RAS 0082-2014-0007. The number of state registration is AAAAA-A18-118012390374-3. Support from the Fundação para a Ciência e a Tecnologia, Portugal (Projects UID/QUI/00100/2013 and PTDC/QEQ-QIN/3967/2014 and Fellowship SFRH/BPD/99533/2014 (to D.S.N.)), is also acknowledged.

#### REFERENCES

- (1) (a) Sanchez, C.; Boissiere, C.; Cassaignon, S.; Chaneac, C.; Durupthy, O.; Faustini, M.; Grosso, D.; Laberty-Robert, C.; Nicole, L.; Portehault, D.; Ribot, F.; Rozes, L.; Sassoey, C. *Molecular Engineering of Functional Inorganic and Hybrid Materials. Chem. Mater.* **2014**, *26*, 221–238. (b) Barboiu, M. Dynamic interactive systems: dynamic selection in hybrid organic–inorganic constitutional networks. *Chem. Commun.* **2010**, *46*, 7466–7476. (c) Tan, J. C.; Cheetham, A. K. Mechanical properties of hybrid inorganic-organic framework materials: establishing fundamental structure-property relationships. *Chem. Soc. Rev.* **2011**, *40*, 1059–1080. (d) Rurack, K.; Martinez-Manez, R., Eds. *The Supramolecular chemistry of organic–inorganic hybrid materials*; Wiley: Hoboken, NJ, 2010. (e) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal–Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105–1125.
- (2) (a) Opanasenko, M.; Shamzhy, M.; Yu, F.; Zhou, W.; Morris, R. E.; Cejka, J. Zeolite-derived hybrid materials with adjustable organic pillars. *Chem. Sci.* **2016**, *7*, 3589–3601. (b) Pospiech, P.; Chojnowski, J.; Mizerska, U.; Makowski, T.; Strzelec, K.; Sienkiewicz, N. Polysiloxane microspheres functionalized with imidazole groups as a palladium catalyst support. *Appl. Organomet. Chem.* **2016**, *30*, 399–407. (c) Kuroda, K.; Shimojima, A.; Kawahara, K.; Wakabayashi, R.; Tamura, Y.; Asakura, Y.; Kitahara, M. Utilization of Alkoxy-silyl Groups for the Creation of Structurally Controlled Siloxane-Based Nanomaterials. *Chem. Mater.* **2014**, *26*, 211–220. (d) Nouredine, A.; Gary-Bobo, M.; Lichon, L.; Garcia, M.; Zink, J. I.; Wong Chi Man, M.; Cattoën, X. *Chem. - Eur. J.* **2016**, *22*, 9624.
- (3) (a) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. Recent Developments in the Chemistry of Cubic Polyhedral Oligosilsesquioxanes. *Chem. Rev.* **2010**, *110*, 2081–2173. (b) Kickelbick, G. Silsesquioxanes. *Functional Molecular Silicon Compounds I*; Springer, 2014; pp 1–28.
- (4) (a) Zhou, H.; Ye, Q.; Xu, J. Polyhedral oligomeric silsesquioxane-based hybrid materials and their applications. *Mater. Chem. Front.* **2017**, *1*, 212–230. (b) Ghanbari, H.; Cousins, B. G.; Seifalian, A. M. A nanocage for nanomedicine: polyhedral oligomeric silsesquioxane (POSS). *Macromol. Rapid Commun.* **2011**, *32*, 1032–1046.
- (5) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. Hetero- and Metallasiloxanes Derived from Silanediols, Disilanols, Silanetriols, and Trisilanols. *Chem. Rev.* **1996**, *96*, 2205–2236. (b) Levitsky, M. M.; Bilyachenko, A. N. Modern concepts and methods in the chemistry of polyhedral metallasiloxanes. *Coord. Chem. Rev.* **2016**, *306*, 235–269. (c) Hanssen, R. W. J. M.; van Santen, R. A.; Abbenhuis, H. C. L. The Dynamic Status Quo of Polyhedral Silsesquioxane Coordination Chemistry. *Eur. J. Inorg. Chem.* **2004**, *2004*, 675–683. (d) Lorenz, V.; Fischer, A.; Gießmann, S.; Gilje, J. W.; Gun'ko, Y.; Jacob, K.; Edelmann, F. T. Disiloxanediolates and polyhedral metallasilsesquioxanes of the early transition metals and f-elements. *Coord. Chem. Rev.* **2000**, *206*–207, 321–368. (e) Edelmann, F. T. Metallasilsesquioxanes. Synthetic and Structural Studies. In *Silicon Chemistry: From the Atom to Extended*

- Systems*; Jutzi, P., Schubert, U., Eds.; Wiley, 2007; pp 383–394.
- (f) Roesky, H. W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. Control of Molecular Topology and Metal Nuclearity in Multimetallic Assemblies: Designer Metallosiloxanes Derived from Silanetriols. *Chem. - Eur. J.* **2004**, *10*, 4106–4114. (g) Bilyachenko, A. N.; Kulakova, A. N.; Levitsky, M. M.; Korlyukov, A. A.; et al. Ionic Complexes of Tetra- and Nonanuclear Cage Cu(II)-phenylsilsesquioxanes: Synthesis and High Activity in Oxidative Catalysis. *ChemCatChem* **2017**, *9*, 4437–4447.
- (6) Feher, F. J. Polyhedral oligometallasilsesquioxanes (POMSS) as models for silica-supported transition-metal catalysts. Synthesis and characterization of (C5Me5)Zr[(Si7O12)(c-C6H11)7]. *J. Am. Chem. Soc.* **1986**, *108*, 3850–3852.
- (7) Nehete, U. N.; Roesky, H. W.; Zhu, H.; Nembenna, S.; Schmidt, H.-G.; Noltemeyer, M.; Bogdanov, D.; Samwer, K. Polyhedral Cobalt(II) and Iron(II) Siloxanes: Synthesis and X-ray Crystal Structure of [(RSi(OH)O2)Co(OPMe3)]4 and [(RSiO3)2(RSi(OH)O2)4(μ3-OH)2Fe8(THF)4] (R = (2,6-iPr2C6H3)N(SiMe3)). *Inorg. Chem.* **2005**, *44*, 7243–7248.
- (8) Edelmann, F. T.; Gun'ko, Y. K.; Giessmann, S.; Olbrich, F.; Jacob, K. Silsesquioxane Chemistry: Synthesis and Structure of the Novel Anionic Aluminosilsesquioxane [HNet3][{Cy7Si7O9-(OSiMe3)O2}2Al]-C6H14 (Cy = c-C6H11). *Inorg. Chem.* **1999**, *38*, 210–211.
- (9) Bilyachenko, A. N.; Dronova, M. S.; Yalymov, A. I.; Korlyukov, A. A.; Shul'pina, L. S.; Arkhipov, D. E.; Shubina, E. S.; Levitsky, M. M.; Kirilin, A. D.; Shul'pin, G. B. New Binuclear Cage-like Copper(II) Silsesquioxane ("Cooling Tower"); Its High Catalytic Activity in Oxidation of Benzene and Alcohols. *Eur. J. Inorg. Chem.* **2013**, *2013*, 5240–5246.
- (10) Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. Studies of copper(I) olefin complexes. Formation constants of copper olefin complexes with 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives. *Inorg. Chem.* **1986**, *25*, 2622–2627.
- (11) Hirotsu, M.; Taruno, S.; Yoshimura, T.; Ueno, K.; Unno, M.; Matsumoto, H. Synthesis and Structures of the First Titanium(IV) Complexes with Cyclic Tetrasiloxide Ligands: Incomplete and Complete Cage Titanosiloxanes. *Chem. Lett.* **2005**, *34*, 1542–1543.
- (12) Bilyachenko, A. N.; Dronova, M. S.; Korlyukov, A. A.; Levitsky, M. M.; Antipin, M. Yu.; Zavin, B. G. Cage-like manganesephenylsiloxane with an unusual structure. *Russ. Chem. Bull.* **2011**, *60*, 1762–1765.
- (13) Oguri, N.; Egawa, Y.; Takeda, N.; Unno, M. Janus-Cube Octasilsesquioxane: Facile Synthesis and Structure Elucidation. *Angew. Chem., Int. Ed.* **2016**, *55*, 9336–9339 and references cited therein.
- (14) Levitsky, M. M.; Zavin, B. G.; Bilyachenko, A. N. Chemistry of metallasiloxanes. Current trends and new concepts. *Russ. Chem. Rev.* **2007**, *76*, 847–866.
- (15) Bilyachenko, A. N.; Dronova, M. S.; Yalymov, A. I.; Lamaty, F.; Bantreil, X.; Martinez, J.; Bizet, C.; Shul'pina, L. S.; Korlyukov, A. A.; Arkhipov, D. E.; Levitsky, M. M.; Shubina, E. S.; Kirillov, A. M.; Shul'pin, G. B. Cage-like Copper(II) Silsesquioxanes: Transmetalation Reactions and Structural, Quantum Chemical, and Catalytic Studies. *Chem. - Eur. J.* **2015**, *21*, 8758–8770.
- (16) (a) Wu, X.-F.; Sharif, M.; Pews-Davtyan, A.; Langer, P.; Ayub, K.; Beller, M. The First ZnII-Catalyzed Oxidative Amidation of Benzyl Alcohols with Amines under Solvent-Free Conditions. *Eur. J. Org. Chem.* **2013**, *2013*, 2783–2787. (b) Gaspa, S.; Porcheddu, A.; De Luca, L. Iron-catalysed oxidative amidation of alcohols with amines. *Org. Biomol. Chem.* **2013**, *11*, 3803–3807. (c) Bantreil, X.; Kanfar, N.; Gehin, N.; Golliard, E.; Ohlmann, P.; Martinez, J.; Lamaty, F. Iron-catalyzed benzamide formation. Application to the synthesis of moclobemide. *Tetrahedron* **2014**, *70*, 5093–5099. (d) Bantreil, X.; Navals, P.; Martinez, J.; Lamaty, F. Iron/Caffeine as a Catalytic System for Microwave-Promoted Benzamide Formation. *Eur. J. Org. Chem.* **2015**, *2015*, 417–422. (e) Bantreil, X.; Fleith, C.; Martinez, J.; Lamaty, F. Copper-Catalyzed Direct Synthesis of Benzamides from Alcohols and Amines. *ChemCatChem* **2012**, *4*, 1922–1925.
- (17) See the [Supporting Information](#) for details on TON and TOF.
- (18) (a) Shul'pin, G. B. Metal-catalyzed hydrocarbon oxygenations in solutions: the dramatic role of additives: a review. *J. Mol. Catal. A: Chem.* **2002**, *189*, 39–66. (b) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Kudinov, A. R.; Mandelli, D. Extremely Efficient Alkane Oxidation by a New Catalytic Reagent H2O2/Os3(CO)12/Pyridine. *Inorg. Chem.* **2009**, *48*, 10480–10482. (c) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Petrovskiy, P. V. Oxidation of alkanes and alcohols with hydrogen peroxide catalyzed by complex Os3-(CO)10(μ-H)2. *Appl. Organomet. Chem.* **2010**, *24*, 464–472. (d) Shul'pin, G. B. Selectivity enhancement in functionalization of C–H bonds: A review. *Org. Biomol. Chem.* **2010**, *8*, 4217–4228. (e) Shul'pin, G. B. New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review. *Catalysts* **2016**, *6*, 50.
- (19) Nesterov, D. S.; Nesterova, O. V.; Pombeiro, A. J. L. Homo- and heterometallic polynuclear transition metal catalysts for alkane C–H bonds oxidative functionalization: Recent advances. *Coord. Chem. Rev.* **2018**, *355*, 199–222.
- (20) Bilyachenko, A. N.; Levitsky, M. M.; Khrustalev, V. N.; Zubavichus, Y. V.; Shul'pina, L. S.; Shubina, E. S.; Shul'pin, G. B. Mild and Regioselective Hydroxylation of Methyl Group in Neocuproine: Approach to an N,O-Ligated Cu6 Cage Phenylsilsesquioxane. *Organometallics* **2018**, *37*, 168–171.
- (21) (a) Bilyachenko, A. N.; Levitsky, M. M.; Korlyukov, A. A.; Khrustalev, V. N.; Zubavichus, Y. V.; Shul'pina, L. S.; Shubina, E. S.; Vologzhanina, A. V.; Shul'pin, G. B. Heptanuclear Cage Cu(II)-Silsesquioxanes. Features of Synthesis, Structure and Catalytic Activity. *Eur. J. Inorg. Chem.* **2018**, *2018*, 2505. (b) Astakhov, G. S.; Bilyachenko, A. N.; Levitsky, M. M.; Korlyukov, A. A.; Zubavichus, Y. V.; Dorovatovskii, P. V.; Khrustalev, V. N.; Vologzhanina, A. V.; Shubina, E. S. *Cryst. Growth Des.* **2018**, DOI: [10.1021/acscgd.8b00778](https://doi.org/10.1021/acscgd.8b00778).