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Alena Kulakova, Alexey N. Bilyachenko, Alexander A. Korlyukov, Lidia S. Shul’Pina, Xavier Bantreil, et al.. A new “bicycle helmet”-like copper(ii),sodiumphenylsilsesquioxane. Synthesis, structure and catalytic activity. Dalton Transactions, 2018, 47 (44), pp.15666-15669. 10.1039/c8dt03209b . hal-03094977

HAL Id: hal-03094977

<https://hal.science/hal-03094977>

Submitted on 4 Jan 2021

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A new “bicycle helmet”-like copper(II), sodiumphenylsilsesquioxane. Synthesis, structure and catalytic activity†

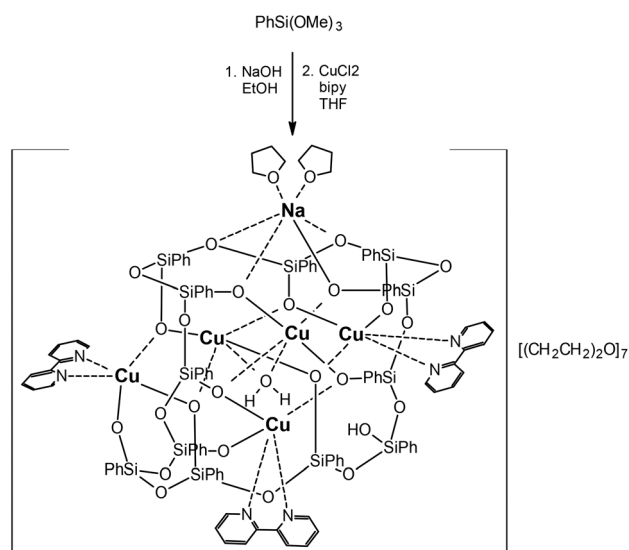
Alena N. Kulakova,^{a,b} Alexey N. Bilyachenko,^{a,b} Alexander A. Korlyukov,^{a,c} Lidia S. Shul’pina,^a Xavier Bantrel,^d Frédéric Lamaty,^d Elena S. Shubina,^e Mikhail M. Levitsky,^a Nikolay S. Ikonnikov^a and Georgiy B. Shul’pin^{*e,f}

A new “bicycle helmet”-like copper(II),sodiumphenylsilsesquioxane $\text{Ph}_{12}\text{Si}_{12}\text{O}_{12}(\text{OH})(\text{O}^-)_{11}\text{Cu}_5\text{Na}(\text{bipy})_3(\text{H}_2\text{O})$ exhibited high catalytic efficiency in two homogeneous reactions: (i) functionalization of C–H compounds; (ii) formation of benzamides from alcohols.

The tremendous popularity of self-assembly reactions aimed at the creation of different types of polyhedral metallacomplexes is explicable by the great efficacy of the underlying methodology.¹ A diverse family of the resultant compounds has been studied widely due to potential material,² biological applications³ and numerous catalytic tasks.⁴ Intriguing opportunities for isolation of cage metallacomplexes could be provided by using non-trivial ligands such as a silicon-based sesquioxane (branched compound of general formula $\text{RSiO}_{1.5}$). Using silsesquioxanes has allowed a family of metalladerivatives (including several examples of heterometallic ones) to be obtained.⁵ In turn, some scholars have reported a “heteroligand” approach⁶ to metallacomplexes of this type, whereby organic ligands (*e.g.*, tris(2-(dimethylamino)ethyl)amine,^{6a} cyclooctenyl,^{6b} 2,2'-bipyridine^{6c,d}) cooperate with the silsesquioxane ligands in the assembling of the cage product. This novel (L_2) type of cage can be especially prospective for their catalytic studies because both ligands (silsesquioxane and

organic) can promote the stability of catalytic species during the reaction. Here, we present our recent observations regarding: self-assembly of Cu(II) ,Na-silsesquioxane in the presence of a widely used 2,2'-bipyridine; determination of the unusual molecular topology of the product; testing of the product as a precatalyst for homogeneous reactions of organic synthesis. Target compound **1** was isolated (in 24% yield) through an interaction between *in situ*-generated Cu,Na-silsesquioxane species and 2,2'-bipyridine (Scheme 1) by varying the ratio between reactants and the nature of solvents. Carrying out the reaction/crystallization in THF favored formation of an earlier, unknown type of cage metallasilsesquioxane molecular topology (Fig. 1, top).

X-ray diffraction indicated that **1** was a mixed metal (Cu_5Na) complex, which crystallized in the $P2_1/c$ space group. This type of nuclearity has not been observed for reported metallasilsesquioxanes.⁷ All copper(II) sites (Fig. S1†)



Scheme 1 General scheme of the self-assembling synthesis of **1**.

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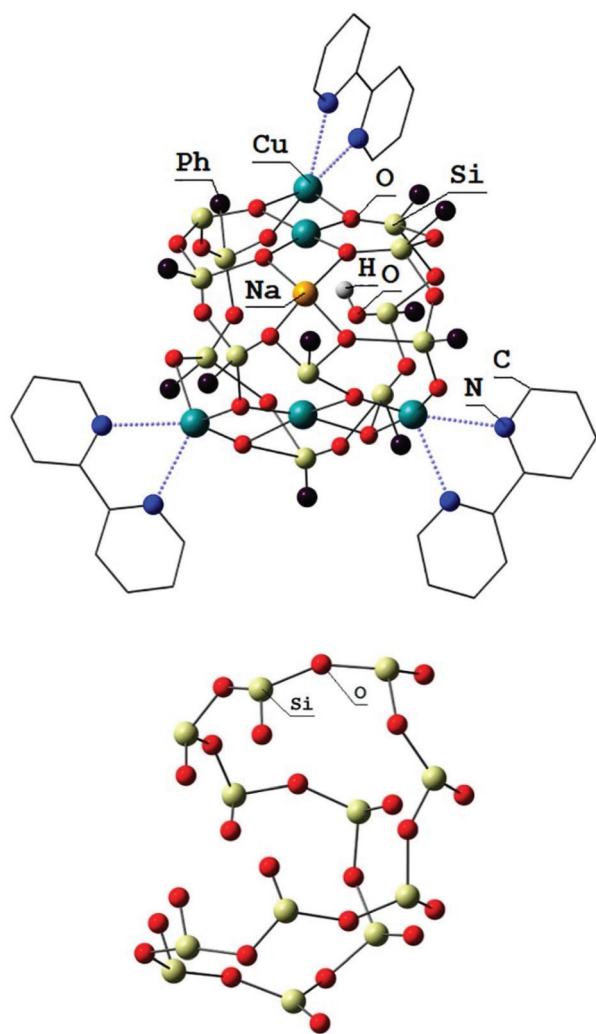


Fig. 1 Top: Molecular structure of **1**. Solvating ligands (THF) and encapsulated species (water) have been removed for clarity. Bottom. Structure of the silsesquioxane ligand in **1**.

possessed a similar distorted square pyramidal pentacoordinated geometry even though three of them were heteroligated (O from silsesquioxane and N from 2,2'-bipyridine). The presence of 2,2'-bipyridine ligands provoked specific packing in the crystal, with two of the three 2,2'-bipyridines participating in π - π stacking interactions of aromatic systems with phenyl groups (Fig. S2[†]). Cu-N bond lengths ranged from 1.996 to 2.214 Å, and Cu-O bond lengths from 1.919 to 2.782 Å. The longest (2.523 Å and 2.782 Å) Cu-O contacts implied the coordination of copper centers to the oxygen atom of encapsulated water (Fig. S3[†]). Such water “capture”, despite some known examples reported for other types of complexes,⁸ is not a widespread feature among the encapsulation abilities of cage silsesquioxanes.⁹

The silsesquioxane skeleton of **1** comprised 12 silicon centers to form one cyclic ligand (Fig. 1, bottom). The topology of the ligand was unprecedented. First, it was important to differentiate this Si₁₂-based ligand from the classical one, of

“globular” geometry, observed many times for Cu(II)-silsesquioxanes.¹⁰ Detailed structural comparison of two of these ligands is given in the ESI (Fig. S4 and Table S1[†]). Here, 11 positive charges from five Cu(II) ions and one Na(I) ion in **1** could not compensate for the 12 negative charges expected from the dodecasilsesquioxane skeleton. Indeed, charge balance became possible due to the presence of hydrogen, which protonated one of the oxygen atoms of the silsesquioxane framework. It elicited a very specific final composition of the ligand: Ph₁₂Si₁₂(O)₁₂(OH)(O⁻)₁₁. The hydroxyl group and encapsulated water molecules formed a system of hydrogen bonds (Table 2, ESI[†]) within the metallasilsesquioxane cage that has rarely (if ever) been observed in compounds of this type. In view of its mono-hydroxyl functionality, only OH-bearing silsesquioxanes belonging to the cubane structural family¹¹ and based-metallacomplexes^{11b,12} have been reported. Logically, these compounds are quite different from **1** in terms of composition and structure.

Being interested in the application of **1** in catalysis, we undertook the first evaluation in homogeneous oxidative reactions. First, oxidations of hydrocarbons with donors of an oxygen atom (*e.g.*, hydrogen peroxide or peroxy acids) constitute an important field of contemporary catalytic chemistry. Complex **1** exhibited high activity in the cyclohexane oxidation with hydrogen peroxide in the absence of any added acid. Thus, the reaction afforded after 2 h at 50 °C oxygenated in 20% yield and turnover number (TON) = 190 (Fig. 2). A comparison of chromatograms obtained before and after addition of PPh₃ (for this method developed by one of our research team, see ref. 13) to the sample indicated that the main product of the reaction, cyclohexyl hydroperoxide, was formed in high concentration because the alcohol/ketone ratio rose dramatically after the reduction, whereas this ratio was ~1 before the reduction. Indeed, cyclohexyl hydroperoxide decomposed in the chromatograph (in the injector and columns) to generate cyclohexanol and cyclohexanone in approximately equal amounts. Unlike many oxidations under different conditions, this reaction gave a much lower product concentration before PPh₃ than after reduction. This finding can be explained by the assumption that cyclohexyl hydroperoxide was not completely reduced with PPh₃ and was not directly detected by our chromatograph. Regioselectivity parameters in the oxidation of *n*-heptane catalyzed by complex **1** [C(1):C(2):C(3):C(4) = 1.0:5.5:5.0:4.5] and the oxidation of *cis*-1,2-dimethylcyclohexane without retention of the configuration (*trans/cis* = 0.9 taking into account the mutual position of the two methyl groups) indicated that this reaction occurred with the participation of free hydroxyl radicals.^{13b}

Complex **1** was also evaluated in the oxidative amidation of benzylic alcohol in the presence of alkylammonium chlorides, calcium carbonate and TBHP (Scheme 2). This reaction allows to circumvent the classical coupling of acids and amines to furnish the corresponding amides (which are present in many organic molecules, including pharmaceutical drugs), but which require at least a stoichiometric amount of coupling agent, which could be toxic and generate a stoichio-

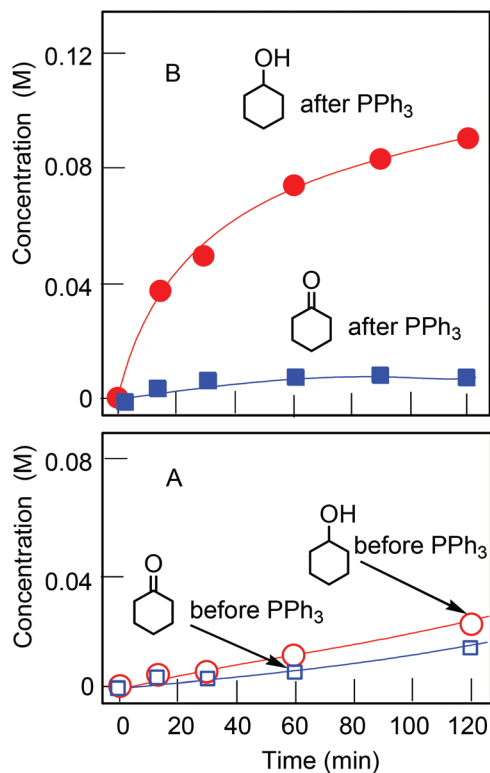
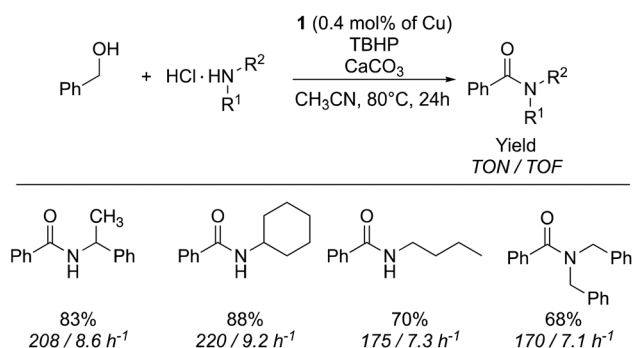


Fig. 2 Accumulation of cyclohexanol and cyclohexanone with time in the cyclohexane (0.46 M) oxidation in acetonitrile with H₂O₂ (50%, aqueous, 1.5 M) catalyzed at 50 °C by compound **1** (5×10^{-4} M). Concentrations measured before (Graph A) and after (Graph B) reduction of the samples with PPh₃ are shown.



Scheme 2 Catalytic activity of **1** in oxidative amidation. Reaction conditions: Ammonium chloride (0.5 mmol), benzyl alcohol (1.0 mmol), CaCO₃ (0.25 mmol), TBHP (5.5 M, 2.5 mmol), **1** (0.4 mol% of Cu), CH₃CN (1 mL), 80 °C, 24 h.

metric quantity of undesired waste.¹⁴ It was originally developed with copper(II) oxide,¹⁵ but the use of cage silsesquioxanes allowed reduction of catalyst loading thanks to their good solubility in organic solvents.¹⁶ With compound **1**, catalyst loading could be reduced to 0.4 mol% of copper and allowed us to obtain good-to-excellent yields of desired amides. The reaction of the hydrochloride salts of α -methylbenzylamine and cyclohexylamine furnished the corresponding amides in

83% and 88% yields, respectively. *N*-Butylbenzamide and *N,N*-dibenzylbenzamide could also be isolated in good yields of 70% and 68%, respectively. TON and turnover frequency (TOF) were calculated, giving values up to 220 and 9.2 h⁻¹ (see ESI† for details on TON and TOF), respectively. If the value of TOF was similar to the one calculated in our seminal report because of the prolonged reaction times with use of **1** compared with CuO (24 h vs. 4 h), TON was increased fivefold, thereby confirming the efficiency of complex **1** in this reaction. Complex **1** was soluble under the reaction conditions, and seemed to be involved as a homogeneous catalyst. Consequently, because of the difficulty of recovery, recycling experiments were not considered at this stage of the project.

Conclusions

We presented a brand-new type of bimetallic (Cu,Na) oxocluster in a heteroligand (phenylsilsesquioxane and 2,2'-bipyridine) surrounding to form a uniquely shaped product Ph₁₂Si₁₂O₁₂(OH)(O⁻)₁₁Cu₅Na(bipy)₃(H₂O). Catalytic tests of this complex showed its high activity in oxidations. Further investigation of this prospective “ligand plus ligand” approach to self-assembly of complicated cage metallastructures and their evaluation in catalysis is currently underway in our research team.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the RUDN University Program “5-100”, the Russian Foundation for Basic Research (17-03-00993, 16-03-00254, 16-53-150008, 16-29-05180, 16-29-05180), French Embassy in Moscow, and University of Montpellier, CNRS (Programme de Recherche Conjoint).

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