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# Combination of Phenylsilsesquioxane and Acetate Ligands as an Approach to a Record High Nuclear $Cu_{13}Na_2$-Cage. Synthesis, Unique Structure, and Catalytic Activity

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Self-assembly synthesis of mixed-ligand (silsesquioxane/acetate) complex allows to isolate record high nuclear copper(II) $Cu_{13}$-cage (**1**). In the presence of two additional sodium ions, a unique molecular architecture, with triple combination of ligands (cyclic and acyclic silsesquioxanes as well as acetates), has been formed. The structure was established by single-crystal X-ray diffraction based on the use of synchrotron radiation. Complex **1** was evaluated as precatalyst in the Baeyer–Villiger oxidation of cyclohexanone towards ε-caprolactone, employing hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) or *m*-chloroperoxybenzoic acid (mCPBA) as oxidants, in an aqueous acidic acetonitrile medium. The direct formation of the lactone from cyclohexane *via* a tandem peroxidative oxidation/Baeyer–Villiger oxidation was also studied. For both substrates, the best results (ε-caprolactone yields up to 100% or 26%, from cyclohexanone or cyclohexane, respectively) were achieved with mCPBA under considerably mild conditions, *i.e.*, conventional heating at 50 °C for 4 h or microwave (MW) irradiation at 80 °C for only 30 minutes.

## Introduction

Impressive molecular and supramolecular aesthetics of cagelike metallasilsesquioxanes (CLMSs) draws a significant attention to this class of metallacomplexes.[1] Wide number of compositions and geometries is explainable for different important functionalities of CLMSs. Several reports discuss magnetic[2] (including single-molecule magnets and spin glasses),[3] and luminescent properties[4] (with examples of ratiometric luminescent thermometers).[3c,5] CLMSs are involved in the development of metal-organic frameworks/coordination polymers[6] and other intriguing materials (semiconductors,[7] photoswitchers,[8] fungicides,[9] intumescent[10] or optoelectrical derivatives[11]). In addition to few examples on CLMS-involved activation of small molecules,[2b,12] significant amount of works are devoted to catalytic properties of CLMSs.[13] These include observations of high activity in Baeyer–Villiger[6c,14] and tandem deacetalization/deketalization-Knoevenagel condensation reactions,[15] synthesis of quinazolinones,[16] or Chan–Evans–Lam couplings.[17] Many of catalytically active CLMSs are complexes with additional organic ligands, providing unusual geometries of cages and high stability during catalyzed reactions.[18] In particular, a family of carboxylate-based copper-CLMSs has been reported,[14,19] including both examples of (*i*) a spontaneous oxidation of alcohol solvents into carboxylates[19a–d] and (*ii*) a directed use of carboxylates as reactants[14.19d–e] Cage structures of all these CLMSs include only copper centers. Taking in mind structural diversity of mixed metal (copper plus alkaline metal ions) CLMSs,[20] we were interested in the preparation of corresponding carboxylate complexes. Here we are presenting our results

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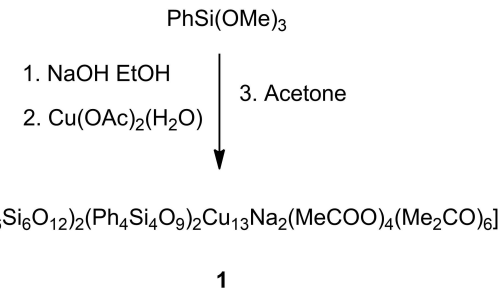
in synthesis, structure elucidation and catalytic activity of the first example of a target, $Cu_{13}Na_2$-based, compound.

## Results and Discussion

### Synthesis and Structure

For the method of synthesis, a reaction of preparation of reactive siloxanolate $[PhSi(O)Na]_n$ species (via alkaline hydrolysis[21] of $PhSi(OMe)_3$ assisted by the action of NaOH in ethanol solution) has been chosen. *In situ* prepared siloxanolate has been brought into interaction with copper(II) acetate monohydrate to replace a part of sodium ions by copper ones (Scheme 1). We failed to isolate a target complex from mother solution but an application of acetone as a key solvate media[22] smoothly provided an intriguing compound $[(Ph_6Si_6O_{12})^{6-}{}_2(Ph_4Si_4O_9)^{6-}{}_2Cu^{2+}{}_{13}Na_2(MeCOO)_4(Me_2CO)_6]$ **1** in 67 % yield. Complex **1** (Figure 1) exhibits several unprecedented unusual compositional and structural features for CLMSs. First of all, $Cu_{13}$ is the highest nuclearity per cage reported for Cu(II)-based CLMSs, superior to a previous record, $Cu_{11}$.[23]

Complex **1** included an unusual set of silsesquioxane ligands: two pairs of $Si_6$-cyclic and $Si_4$-acyclic ones (Figure 2, top). This allows to form an intriguing metaloxide core of $Cu^{II}{}_{13}Na^{I}{}_2$ nuclearity (Figure 2, bottom). In sum, it provides 28 positive charges, which could not be compensated by 24 negative charges from four silsesquioxane ligands (two $(Ph_6Si_6O_{12})^{6-}$ cycles and two $(Ph_4Si_4O_9)^{6-}$ acyclic species). Due to this, two pair of acetate ligands additionally coordinate two opposite copper ions. Each sodium center in **1** is additionally solvated by acetone molecule. In sum, this type of molecular geometry of **1** could be described as a fusion of two unfinished $Si_{10}Cu_6Na$ sandwich fragments (Figure S3) via central thirteenth copper ion. The nine "internal" copper atoms surrounding only by the silsesquioxane ligands have a square-planar coordination, while the four "external" copper atoms bound to the silsesquioxane and acetate ligands and acetone molecules adopt a tetragonal-pyramidal environment.




**Scheme 1.** Synthesis of $Cu_{13}Na_2$-phenylsilsesquioxane/acetate cage **1**.

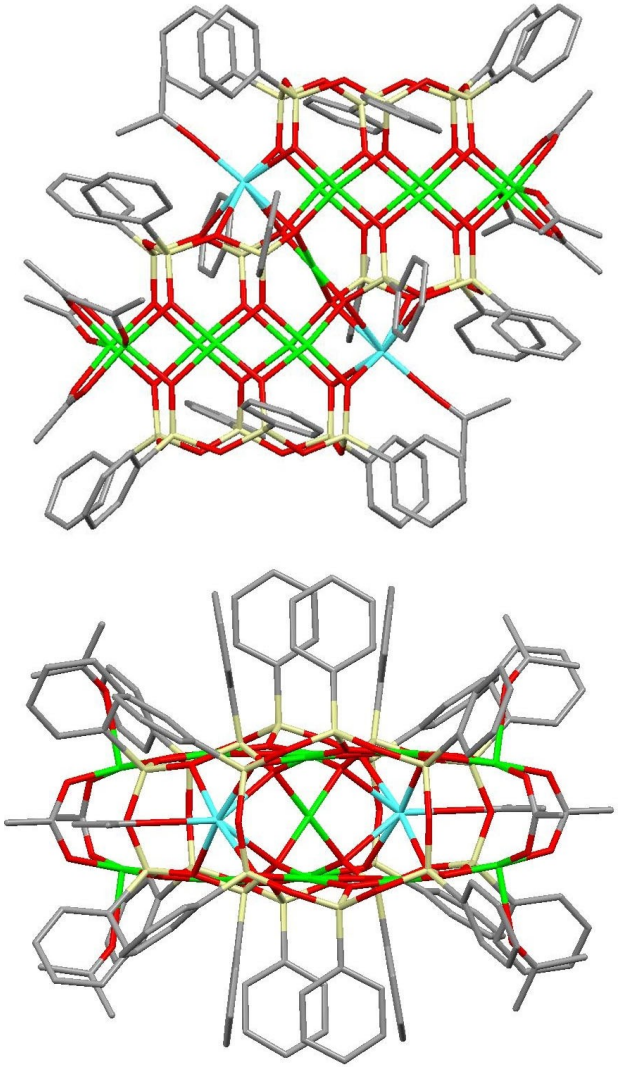


**Figure 1.** Two projections of molecular structure of $Cu_{13}Na_2$-phenylsilsesquioxane/acetate cage **1**. Color code: Si, yellow; O, red; Cu, green; Na, aqua; C, gray. Hydrogen atoms are omitted for clarity.

### Catalytic Activity

Complex **1** is soluble in different polar (acetonitrile, THF, DMF, DMSO) and aromatic (benzene, toluene) organic solvents. It provides an opportunity to study complex **1** as precatalyst in homogeneous reaction of organic synthesis. Compound **1** was tested in the Baeyer–Villiger (B–V) oxidation of cyclohexanone and tandem cyclohexane oxidation/B–V oxidation of cyclohexanone, using three different oxidants [aqueous hydrogen peroxide ($H_2O_2$), aqueous *tert*-butyl hydroperoxide (TBHP) or *m*-chloroperoxybenzoic acid (mCPBA)], and employing 1 (or 0.5, when mCPBA was used) mmol of substrate and a catalyst loading of 0.2 (or 0.4) mol%. The stable and polar acetonitrile was used as solvent due to its ability to solubilize both substrates, the oxidant and the metal catalyst, as well as on account of its resistance to oxidation.

A heptanuclear copper(II)-phenylsilsesquioxane bearing benzoate ligands, $(Ph_5Si_5O_{10})_2(PhCOO)_4Cu_7$ (**A**),[24] was thor-

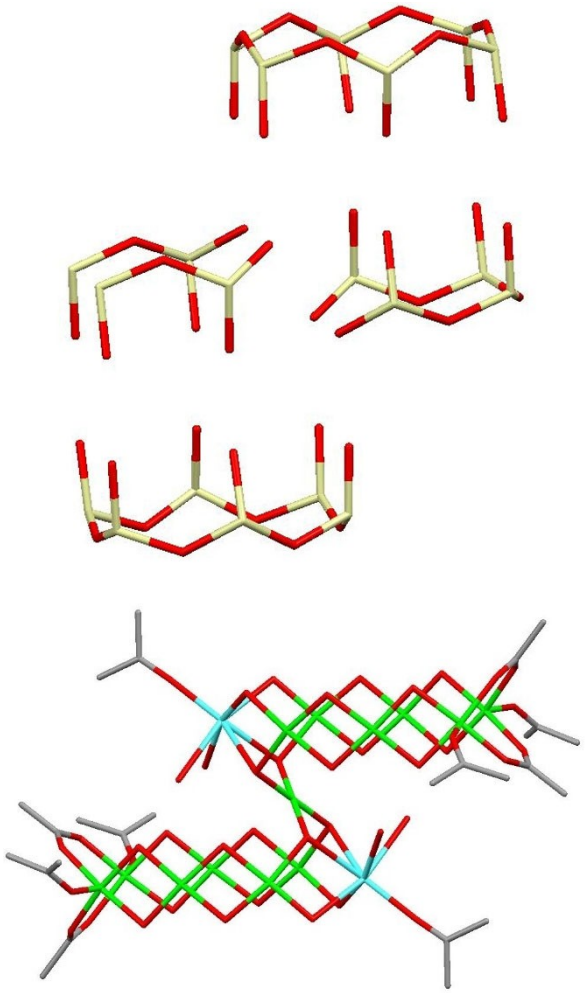


**Figure 2.** Top. Structures of two pair ($Si_6$ cyclic and $Si_4$ acyclic) ligands in **1**. Bottom. $Cu_{13}Na_2$ metal core in **1**. Color code the same as for Figure 1.

oughly studied as catalyst in these B–V oxidation reactions (full results disclosed in Tables S2–S5, Supporting Information) and therefore the following optimal conditions were explored with the $Cu_{13}Na_2$-complex **1**: (i) conventional heating at 50 °C, 4 h reaction time and $HNO_3$ as promoter; and (ii) microwave (MW)-irradiation at 70 or 80 °C for 0.5 h, employing nitric acid as co-catalyst and using $H_2O_2$ (2 mmol), TBHP (5 mmol) or mCPBA (1 or 2 mmol) as oxidants.

### *Cyclohexanone as Substrate*

The results obtained in the B–V oxidation of cyclohexanone are summarized in Table 1.

When employing mCPBA as oxidant (Table 1, entries 3 to 5), 90 to 100% yields of ε-caprolactone were achieved under the studied conditions (conventional heating at 50 °C or MW-irradiation at 70 or 80 °C). However, no ε-caprolactone was detected when using $H_2O_2$ as oxidant (with MW-irradiation at 70 °C for 30 minutes – Table 1, entry 1) but an interesting yield of 29% (entry 2) was registered upon usage of TBHP, under similar experimental conditions (something that was not accomplished with other Cu-CLMSs that were also studied[6c,14]).

### *Cyclohexane as Substrate*

Regarding the tandem cyclohexane oxidation/Baeyer–Villiger oxidation of cyclohexanone, the Table 2 depicts the results (yields of KA oil – mixture of cyclohexanone and cyclohexanol – and ε-caprolactone, as well as TONs and TOFs recorded for the lactone formation) achieved for this system.

When using mCPBA, yields of 25–26% in ε-caprolactone were attained with conventional heating at 50 °C for a longer period (4 h) or upon MW-irradiation at a higher temperature (80 °C) although only in 0.5 h (Table 2, entries 3 and 5, respectively). Interestingly, 5–7% of KA oil was obtained in these conditions but a slightly higher value of 12% (entry 4) was recorded when the MW-assisted reaction took place in a lower temperature (70 °C).

When employing $H_2O_2$ or TBHP (Table 2, entries 1–2), no lactone was formed or only in a low yield (6%, entry 2), whereas the KA oil yield achieved a remarkable value of 55% (with predominance of cyclohexanone – 45%) with TBHP oxidant. These observations are consistent with the involvement of cyclohexanone in the formation of the lactone and the required use of a higher temperature and stronger oxidant for the promotion of the B–V reaction following the cyclohexane oxidation.

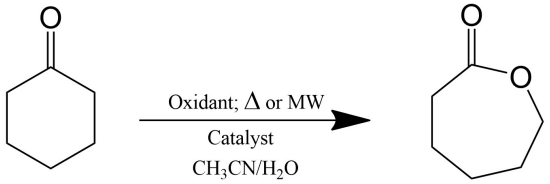
### *Blank Tests and Common Cu(II) Salts*

To further assess the catalytic potential of the $Cu_{13}Na_2$-phenyl-silsesquioxane **1**, blank tests (no metal source added) and experiments using common Cu(II) salts instead, namely $CuCl_2$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ (complex metal precursor), were performed with mCPBA (1 or 2 mmol) for: (i) conventional heating at 50 °C for 4 h; and (ii) MW irradiation at 70 °C for 0.5 h (Tables 1 and 2, entries 6–13).

The blank tests gave 70% and 79% of ε-caprolactone for conventional heating and MW-irradiation, respectively, when employing cyclohexanone as substrate (Table 1, entries 6 and 7), therefore pointing to the involvement of a non-catalyzed pathway leading to the lactone formation, as will be further discussed. Using cyclohexane as substrate (Table 2, entries 6–7), only 1% of lactone and 1–2% of KA oil were obtained for experimental conditions (i) and (ii). These results are clearly below those attained with the compound **1** under similar conditions.

Similarly, the copper(II) salts exhibited a lower catalytic performance in the studied Baeyer–Villiger oxidation reactions, with maximum yields of 77–86% (Table 1, entries 10 and 13; for copper(II) acetate) or 2% (Table 2, entries 8, 9 and 11) regarding the lactone formation from cyclohexanone or cyclohexane, respectively, although similar yields of KA oil were obtained with the cupric chloride in the MW-assisted experiment.

**Table 1.** Baeyer–Villiger oxidation of cyclohexanone by $H_2O_2$, TBHP or mCPBA catalyzed by the compound **1** or Cu(II) salts.




| | Method | Catalyst | Oxidant | Peroxide loading/mmol | t/°C | Time/h | Yield/% | TON[a] | TOF[b]/$h^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | MW irradiation | 1 | $H_2O_2$ | 2 | 70 | 0.5 | 0 | 0 | 0 |
| **2** | MW irradiation | 1 | TBHP | 5 | 70 | 0.5 | 29 | 145 | 290 |
| **3** | Normal heating | 1 | mCPBA + $O_2$ | 1 | 50 | 4 | 100 | 250 | 63 |
| **4** | MW irradiation | 1 | mCPBA | 2 | 70 | 0.5 | 90 | 225 | 450 |
| **5** | MW irradiation | 1 | mCPBA | 2 | 80 | 0.5 | 100 | 250 | 500 |
| **6** | Normal heating | None | mCPBA + $O_2$ | 1 | 50 | 4 | 70 | N/A | N/A |
| **7** | MW irradiation | None | mCPBA | 2 | 70 | 0.5 | 79 | N/A | N/A |
| **8** | Normal heating | $CuCl_2$ | mCPBA + $O_2$ | 1 | 50 | 4 | 74 | 185 | 46 |
| **9** | Normal heating | $Cu(NO_3)_2 \cdot 3H_2O$ | mCPBA + $O_2$ | 1 | 50 | 4 | 63 | 158 | 40 |
| **10** | Normal heating | $Cu(CH_3COO)_2 \cdot H_2O$ | mCPBA + $O_2$ | 1 | 50 | 4 | 77 | 193 | 48 |
| **11** | MW irradiation | $CuCl_2$ | mCPBA | 2 | 70 | 0.5 | 72 | 180 | 360 |
| **12** | MW irradiation | $Cu(NO_3)_2 \cdot 3H_2O$ | mCPBA | 2 | 70 | 0.5 | 62 | 155 | 310 |
| **13** | MW irradiation | $Cu(CH_3COO)_2 \cdot H_2O$ | mCPBA | 2 | 70 | 0.5 | 86 | 215 | 430 |

*Reaction conditions:* cyclohexanone (1 mmol for $H_2O_2$ and TBHP oxidants; 0.5 mmol for mCPBA), catalyst (2 μmol), $HNO_3$ (25 μmol), in acetonitrile (950 μL). [a] TON, turnover number: (moles of product)/(mole of catalyst). [b] TOF, turnover frequency: TON/time (h). N/A – Not applicable.

### *Comparison with the $Cu_7$-Silsesquioxane/Benzoate Complex A*

The $Cu_{13}Na_2$-phenylsilsesquioxane compound **1** is more active as catalyst towards the ε-caprolactone formation: (i) when using cyclohexanone as substrate, yields ranging between 90–100% were attained (Table 1, entries 3–5), while with compound **A** 84 to 100% were recorded (the quantitative reaction only upon MW irradiation at 80 °C – Table 3, entry 3); and, in particular, (ii) when starting from cyclohexane, yields up to 25–26% of lactone were registered with **1** (Table 2, entries 3 and 5) in comparison with the maximum of 19% for **A** (also in the MW-assisted reaction at 80 °C – Table 3, entry 6).

The higher nuclearity of the complex **1** may account for such an improved catalytic performance. Indeed, the metal sites, due to their Lewis acidic character, play a pivotal role in the activation of both substrate (ketone carbonyl group) and oxidant (promotion of the electrophilicity of the ketone carbonyl group and of the peroxide moiety). It is expected[6c,14,25] to occur, upon nucleophilic attack of the peroxide to the carbonyl group of the coordinated ketone, the formation of a 5-membered peroxymetallacyclic intermediate. Rearrangement of this species involving heterolytic O–O bond cleavage at the peroxide group, C–C bond cleavage at the cyclohexyl moiety with C–O bond formation upon insertion of the peroxy oxygen atom leads to the desired lactone product.

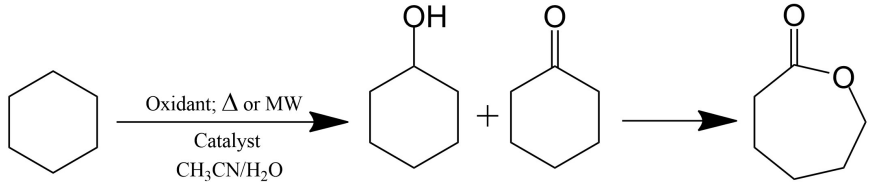
On the other hand, the non-catalyzed Baeyer–Villiger reaction using a peracid as oxidant has a well-known mechanism involving the formation of a related (to the peroxymetallacyclic intermediate above) "Criegee intermediate" upon nucleophilic attack of the peracid to the activated by protonation carbonyl moiety, i.e. C=O(+)H, of the substrate. Its rearrangement (see above) yields the oxidized product.[6c,14,25]

### *Comparison with other Copper Catalytic Systems*

The results obtained with the $Cu_{13}Na_2$-phenylsilsesquioxane **1** are in line with the ones registered for the coordination polymer $Cu_5Cs_4$-CLMS:[6c] quantitative yields of ε-caprolactone when using cyclohexanone as substrate (normal heating at 50 °C during 4 h or MW irradiation for 0.5 h at 80 °C; although a 100% of yield was also attained at lower temperatures with MW with the pentanuclear Cu(II) compound). Upon employment of cyclohexane as starting material, yields of 17–19% and 25–26% were recorded for the $Cu_5Cs_4$- and $Cu_{13}Na_2$-phenylsilsesquioxanes, respectively (under the experimental conditions depicted above). These values are slightly higher than the ones obtained with a $Cu_6$-phenylsilsesquioxane/acetate complex:[14] 88 to 100% of lactone from cyclohexanone and 4–16% directly from the analogous alkane, by using mCPBA oxidant as well and under similar experimental conditions (heating method, temperature and reaction time).

Taking into consideration other copper homogeneous catalytic systems,[26] different conditions were used (longer reaction times at room temperature, in a benzene or toluene $H_2O$-saturated medium) and the so-called "sacrificial aldehyde method" (using $O_2$ + aldehyde as oxidant) was applied, leading to 19–34% of conversion. A Cu(II) complex bearing a Schiff-

**Table 2.** Tandem cyclohexane oxidation/Baeyer–Villiger oxidation of cyclohexanone by $H_2O_2$, TBHP or mCPBA catalyzed by the compound **1** or Cu(II) salts.




| | Method | Catalyst | Oxidant | Peroxide loading/ mmol | t/ °C | Time/ h | Yield/% KA oil (ket + alc) | Yield/% lactone | TON[a] (lactone) | TOF[b]/ $h^{-1}$ (lactone) |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | MW irradiation | 1 | $H_2O_2$ | 2 | 70 | 0.5 | 8 (4 + 4) | 0 | 0 | 0 |
| **2** | MW irradiation | 1 | TBHP | 5 | 70 | 0.5 | 55 (45 + 10) | 6 | 30 | 60 |
| **3** | Normal heating | 1 | mCPBA + $O_2$ | 1 | 50 | 4 | 5 (3 + 2) | 25 | 63 | 16 |
| **4** | MW irradiation | 1 | mCPBA | 2 | 70 | 0.5 | 12 (7 + 5) | 2 | 5 | 10 |
| **5** | MW irradiation | 1 | mCPBA | 2 | 80 | 0.5 | 7 (4 + 3) | 26 | 65 | 130 |
| **6** | Normal heating | None | mCPBA + $O_2$ | 1 | 50 | 4 | 1 (0 + 1) | 1 | N/A | N/A |
| **7** | MW irradiation | None | mCPBA | 2 | 70 | 0.5 | 2 (1 + 1) | 1 | N/A | N/A |
| **8** | Normal heating | $CuCl_2$ | mCPBA + $O_2$ | 1 | 50 | 4 | 3 (1 + 2) | 2 | 5 | 1 |
| **9** | Normal heating | $Cu(NO_3)_2 \cdot 3H_2O$ | mCPBA + $O_2$ | 1 | 50 | 4 | 3 (1 + 2) | 2 | 5 | 1 |
| **10** | Normal heating | $Cu(CH_3COO)_2 \cdot H_2O$ | mCPBA + $O_2$ | 1 | 50 | 4 | 0 | 1 | 3 | 1 |
| **11** | MW irradiation | $CuCl_2$ | mCPBA | 2 | 70 | 0.5 | 8 (2 + 6) | 2 | 5 | 10 |
| **12** | MW irradiation | $Cu(NO_3)_2 \cdot 3H_2O$ | mCPBA | 2 | 70 | 0.5 | 0 | 0 | 0 | 0 |
| **13** | MW irradiation | $Cu(CH_3COO)_2 \cdot H_2O$ | mCPBA | 2 | 70 | 0.5 | 3 (0 + 3) | 0 | 0 | 0 |

*Reaction conditions:* cyclohexane (1 mmol for $H_2O_2$ and TBHP oxidants; 0.5 mmol for mCPBA), catalyst (2 μmol), $HNO_3$ (25 μmol), in acetonitrile (950 μL).
[a] TON, turnover number: (moles of product)/(mole of catalyst). [b] TOF, turnover frequency: TON/time (h). N/A – Not applicable.

base ligand[27] was also evaluated as a homogeneous catalyst for the conversion of cyclopentanone by aqueous $H_2O_2$ upon reaction in $CH_3OH$ (70 °C for 6 h), which led to 45% of substrate conversion and 83% of lactone selectivity.

Concerning the supported/heterogeneous copper systems,[26c–d,27,28] in general medium to high substrate conversions were achieved by $H_2O_2$ or $O_2$/benzaldehyde oxidants, with selectivities of the lactone above 80%. However, when employing a Cu(II) complex enslaved in Zeolite-Y or $Cu(NO_3)_2 \cdot 3H_2O$ supported in MIL-101(Cr), much lower yields or conversions (around 20%) were attained.

## Conclusions

Self-assembly of acetate-based cage silsesquioxane complex with pair combination of metal ions – transition, Cu(II), and alkaline, Na(I), ones – allows to isolate a compound with the highest reported nuclearity among copper(II) silsesquioxanes, $Cu_{13}Na_2$. Specific structure of complex is realized with double set of silsesquioxanes – two cyclic and two acyclic ligands. Four copper centers are additionally ligated by four acetate moieties. Combination of silsesquioxane and acetate ligands is also convenient for preparing other types of cages (for $Cu_8$-complex **2** and $Cu_7$-complex **3** see SI). Compound **1** exhibits good activity as precatalyst in the Baeyer–Villiger oxidation of cyclohexanone and in the tandem cyclohexane oxidation/B–V oxidation of the produced cyclohexanone to ε-caprolactone, by employing *m*-chloroperoxybenzoic acid as oxidant in an acidic ($HNO_3$) acetonitrile aqueous medium, supporting the noteworthy role of multicopper-silsesquioxanes as catalysts, under considerably mild conditions, for this kind of reactions. Of particular interest is the possibility of using cyclohexane as the starting material, in a single-pot and more sustainable process leading to the

**Table 3.** Baeyer–Villiger oxidation reactions of cyclohexanone or cyclohexane by mCPBA catalyzed by the $Cu_7$-silsesquioxane/benzoate complex **A** (selected results).

| | Method | Substrate | Oxidant | Peroxide loading/ mmol | Promoter | t/ °C | Time/ h | Yield/% KA oil (ket + alc) | Yield/% lactone | TON[a] (lactone) | TOF[b]/ $h^{-1}$ (lactone) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | Normal heating | cyclohexanone | mCPBA + $O_2$ | 1 | $HNO_3$ | 50 | 4 | – | 84 | 210 | 53 |
| **2** | MW irradiation | cyclohexanone | mCPBA | 2 | $HNO_3$ | 70 | 0.5 | – | 93 | 232 | 465 |
| **3** | MW irradiation | cyclohexanone | mCPBA | 2 | $HNO_3$ | 80 | 0.5 | – | 100 | 250 | 500 |
| **4** | Normal heating | cyclohexane | mCPBA + $O_2$ | 1 | $HNO_3$ | 50 | 4 | 4 (2 + 2) | 6 | 15 | 4 |
| **5** | MW irradiation | cyclohexane | mCPBA | 2 | $HNO_3$ | 70 | 0.5 | 7 (3 + 4) | 9 | 23 | 45 |
| **6** | MW irradiation | cyclohexane | mCPBA | 2 | $HNO_3$ | 80 | 0.5 | 7 (3 + 4) | 19 | 48 | 95 |

Reaction conditions: cyclohexane (1 or 0.5 mmol; 0.5 mmol for mCPBA loading $\geq$ 1 mmol), catalyst (2 μmol), promoter (25 μmol), in acetonitrile (950 μL). [a] TON, turnover number: (moles of product)/(mole of catalyst). [b] TOF, turnover frequency: TON/time (h).

desired lactone, thus overcoming the need of isolating the cyclohexanone/cyclohexanol (KA oil) intermediates.

Convenience of preparation of carboxylate derivatives of cage metallasilsesquioxanes points at a significant potential of this chemistry. Further investigations of synthesis and functionalities of this intriguing class of metallacomplexes are on their way in our groups.

## Supporting Information

The authors have cited additional references within the Supporting Information.[29–32]

Deposition Numbers 2384827 (for 1), 2384828 (for 2), 2384829 (for 3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe http://www.ccdc.cam.ac.uk/structures.

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## *Conflict of Interests*

The authors declare no conflict of interest.

## *Data Availability Statement*

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** metallasilsesquioxanes · copper · acetates · Baeyer–Villiger oxidation · ε-caprolactone

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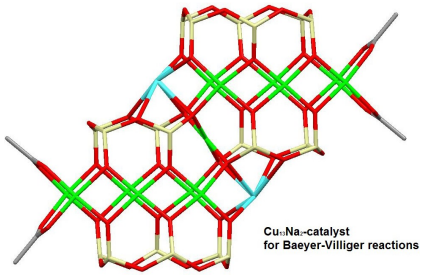
# RESEARCH ARTICLE

Self-assembly synthesis of silsesquioxane/acetate complex allows to isolate record high nuclear copper(II) $Cu_{13}$-cage. Complex was evaluated as pre-catalyst in the Baeyer–Villiger oxidation of cyclohexanone towards ε-caprolactone. The direct formation of the lactone from cyclohexane via a tandem peroxidative oxidation/Baeyer–Villiger oxidation was also studied.

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1 – 8

**Combination of Phenylsilsesquioxane and Acetate Ligands as an Approach to a Record High Nuclear $Cu_{13}Na_2$-Cage. Synthesis, Unique Structure, and Catalytic Activity**