

Supplemental material

for

Rational (supra)molecular design and catalytic activity of cage-like Cu₄-based phenylsilsesquioxanes

by

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Experimental Section

General

All reagents and solvents (p.a. grade) were obtained from commercial sources and used without further purification. RbOH and CsOH were used as 50% w/w water solutions. Elemental analyses were carried out with an XRF spectrometer VRA-30 and Eurovector EA-3000 analyzer. Powder pattern was measured on a Tongda TDM-20 diffractometer at room temperature (CuK α radiation, Ni filter, $\theta/2\theta$ scan from 5° to 30°). IR spectra (KBr pellets) of the compounds were measured on a Shimadzu IRPrestige 21 FT-IR spectrophotometer equipped with an MCT detector using a Miracle single reflection ATR unit by Pike. Figure S4 is to exemplify the view of spectrum for **12**. UV-Vis spectra (10 mm optical path length, ethanol solutions) were recorded on a Cary 50 spectrophotometer. Figure S5 is to exemplify the view of spectrum for **12**.

Synthesis of **1**

1 g (5 mmol) of PhSi(OMe)₃ and 0.21 g (5 mmol) of LiOH·H₂O were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of CuCl₂ was added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave a crystalline material in 3-4 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield.

Anal. Calcd. for (C₆H₅)₁₂(Si₁₂O₂₄)Li₄Cu₄: Cu, 13.18; Li, 1.44; Si, 17.48. Found: Cu, 13.11; Li, 1.39; Si, 13.10. Yield: 0.56 g (70%)

Synthesis of **2**

1 g (5 mmol) of PhSi(OMe)₃ and 0.2 g (5 mmol) of NaOH were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of CuCl₂ was added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave a crystalline material in 3-4 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield.

Anal. Calcd. for (C₆H₅)₁₂(Si₁₂O₂₄)Na₄Cu₄: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.73; Na, 4.57; Si, 16.86. Yield: 0.61 g (73%)

Syntheses of **3-6a**

In a typical procedure, 0.1 g of dried complex **2** were mixed with the corresponding solvent(s), see below for details. Solutions were stirred for 30 minutes upon heating (not reflux), followed by centrifugation of the precipitates. Crystallization of filtrates by slow evaporation gave crystalline materials in a period of ~3-7 days, including single crystals that were used for X-ray diffraction studies. The rest of crystalline materials were dried in vacuum to calculate yield. Complexes **6-6a** were isolated during parallel runs of the reaction.

For complex **3**. Solvent – acetone (30 ml). Anal. Calcd. for (C₆H₅)₁₂(Si₁₂O₂₄)Na₄Cu₄: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.70; Na, 4.54; Si, 16.88. Yield: 0.07 g (69%)

For complex **4**. Solvents – ethanol/acetonitrile (15 ml/15 ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.71; Na, 4.55; Si, 16.83. Yield: 0.06 g (58%)

For complex **5**. Solvents – ethanol/acetone (15 ml/15 ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.70; Na, 4.51; Si, 16.85. Yield: 0.07 g (68%)

For complex **6**. Solvents – ethanol/diethyl ether (15 ml/15 ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.67; Na, 4.54; Si, 16.86. Yield: 0.06 g (62%)

For complex **6a**. Solvents – ethanol/diethyl ether (15 ml/15 ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.70; Na, 4.55; Si, 16.82. Yield: 0.06 g (60%)

Syntheses of **7-8**

In a typical procedure, 1 g (5 mmol) of $PhSi(OMe)_3$ and 0.2 g (5 mmol) of NaOH were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of $CuCl_2$ and 10 ml of water were added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate in a fridge gave a crystalline material in 5-7 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield. Complexes **7-8** were isolated during parallel runs of the reaction.

For complex **7**. Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.71; Na, 4.59; Si, 16.84. Yield: 0.43 g (52%)

For complex **8**. Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})Na_4Cu_4$: Cu, 12.76; Na, 4.62; Si, 16.92. Found: Cu, 12.66; Na, 4.55; Si, 16.79. Yield: 0.48 g (58%)

Synthesis of **9**

1 g (5 mmol) of $PhSi(OMe)_3$ and 0.28 g (5 mmol) of KOH were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of $CuCl_2$ was added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave a crystalline material in 3-4 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield.

Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})K_4Cu_4$: Cu, 12.36; K, 7.60; Si, 16.39. Found: Cu, 12.30; K, 7.55; Si, 16.32. Yield: 0.61 g (68%)

Syntheses of **10-12**

In a typical procedure, 0.1 g of dried complex **9** were mixed with the corresponding solvent(s), see below for details. Solution was stirred for 30 minutes upon heating (not reflux), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave crystalline material in a period of ~5 days, including single crystals that were used for X-ray diffraction studies. The rest of crystalline material was dried in vacuum to calculate yield.

For complex **10**. Solvents – DMF/MeOH/EtOH (15 ml/10ml/10ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})K_4Cu_4$: Cu, 12.36; K, 7.60; Si, 16.39. Found: Cu, 12.22; K, 7.49; Si, 16.30. Yield: 0.06 g (62%)

For complex **11**. Solvents – diethyl ether/acetonitrile/water (15 ml/10 ml/5ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})K_4Cu_4$: Cu, 12.36; K, 7.60; Si, 16.39. Found: Cu, 12.27; K, 7.51; Si, 16.33. Yield: 0.06 g (60%)

For complex **12**. Solvent – acetone (30 ml). Anal. Calcd. for $(C_6H_5)_{12}(Si_{12}O_{24})K_4Cu_4$: Cu, 12.36; K, 7.60; Si, 16.39. Found: Cu, 12.29; K, 7.53; Si, 16.30. Yield: 0.07 g (73%)

Syntheses of **13-13a**

1 g (5 mmol) of PhSi(OMe)_3 and 0.52 g (5 mmol) of RbOH were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of CuCl_2 was added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave a crystalline material in 4-5 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield. Complexes **13-13a** were isolated during parallel runs of the reaction.

For complex **13**. Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Rb}_4\text{Cu}_4$: Cu, 11.34; Rb, 15.25; Si, 15.03. Found: Cu, 11.28; Rb, 15.14; Si, 14.95. Yield: 0.60 g (63%)

For complex **13a**. Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Rb}_4\text{Cu}_4$: Cu, 11.34; Rb, 15.25; Si, 15.03. Found: Cu, 11.25; Rb, 15.15; Si, 14.90. Yield: 0.60 g (60%)

Syntheses of **14-15**

In a typical procedure, 0.1 g of dried complex **11** were mixed with the corresponding solvent, see below for details. Solutions were stirred for 30 minutes upon heating (not reflux), followed by centrifugation of the precipitates. Crystallization of filtrates by slow evaporation gave crystalline materials in a period of ~5-7 days, including single crystals that were used for X-ray diffraction studies. The rest of crystalline materials were dried in vacuum to calculate yield.

For complex **14**. Solvent – DMF (30 ml). Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Rb}_4\text{Cu}_4$: Cu, 11.34; Rb, 15.25; Si, 15.03. Found: Cu, 11.25; Rb, 15.11; Si, 14.91. Yield: 0.07 g (67%)

For complex **15**. Solvent – acetone (30 ml). Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Rb}_4\text{Cu}_4$: Cu, 11.34; Rb, 15.25; Si, 15.03. Found: Cu, 11.25; Rb, 15.11; Si, 14.91. Yield: 0.07 g (71%)

Syntheses of **16-17**

1 g (5 mmol) of PhSi(OMe)_3 and 0.75 g (5 mmol) of CsOH were heated at reflux in 40 ml of ethanol for 2.5 h. Then, 0.22 g (1.68 mmol) of CuCl_2 was added. The resulting mixture was stirred without heating overnight (12 h), followed by centrifugation of the precipitate. Crystallization of filtrate by slow evaporation gave a crystalline material in 4-5 days, including single crystals that were used for X-ray diffraction study. The rest of crystalline material was dried in vacuum to calculate yield. Complexes **16-17** were isolated during parallel runs of the reaction.

For complex **16**. Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Cs}_4\text{Cu}_4$: Cs, 21.86; Cu, 10.45; Si, 13.86. Found: Cs, 21.78; Cu, 10.40; Si, 13.81. Yield: 0.74 g (72%)

For complex **17**. Anal. Calcd. for $(\text{C}_6\text{H}_5)_{12}(\text{Si}_{12}\text{O}_{24})\text{Cs}_4\text{Cu}_4$: Cs, 21.86; Cu, 10.45; Si, 13.86. Found: Cs, 21.86; Cu, 10.45; Si, 13.86. Yield: 0.62 g (61%)

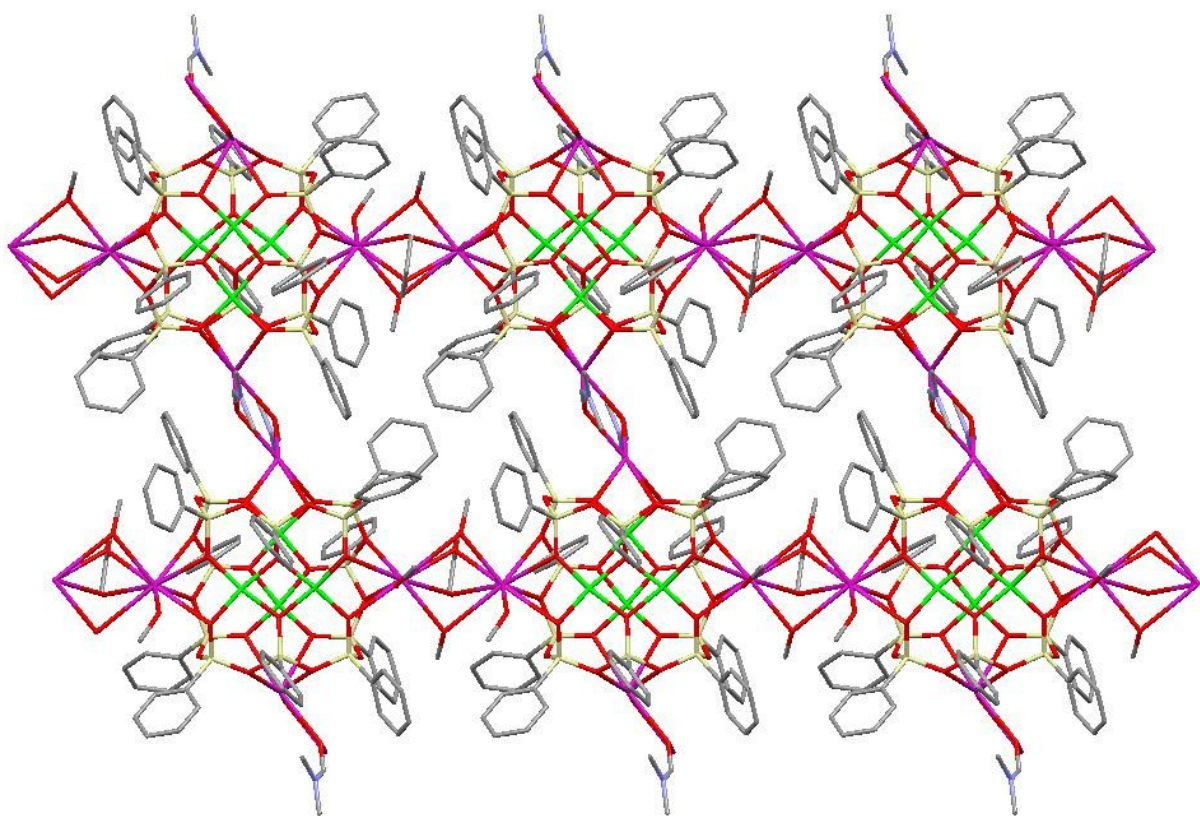


Figure S1. 2D coordination polymer **10**. Color code: green Cu; yellow Si; red O; grey C; magenta K

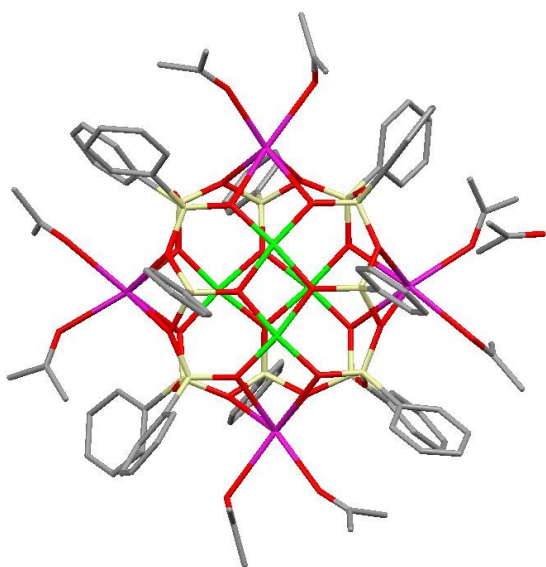


Figure S2. Molecular structure of **12**. Color code: green Cu; yellow Si; red O; grey C; magenta K. Intracage K...K distances are equal to 9.347 Å and 9.387 Å.

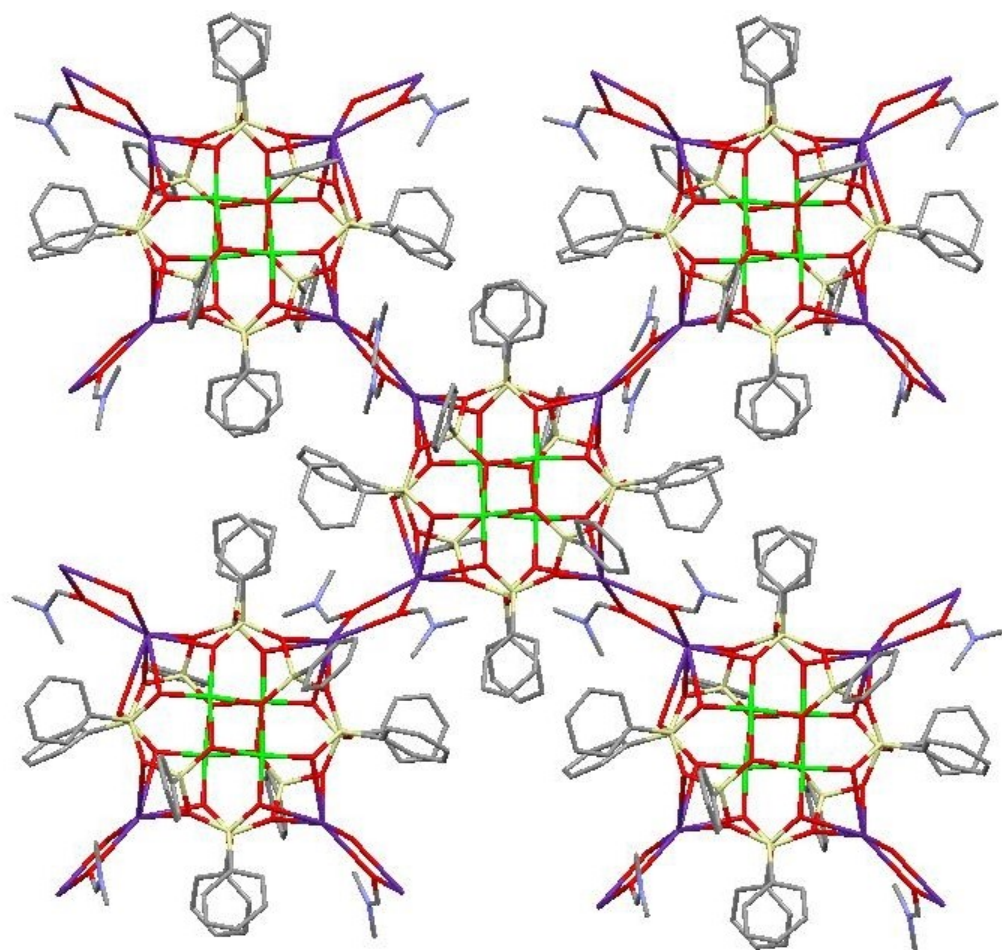


Figure S3. View of structural unit of complex 14.

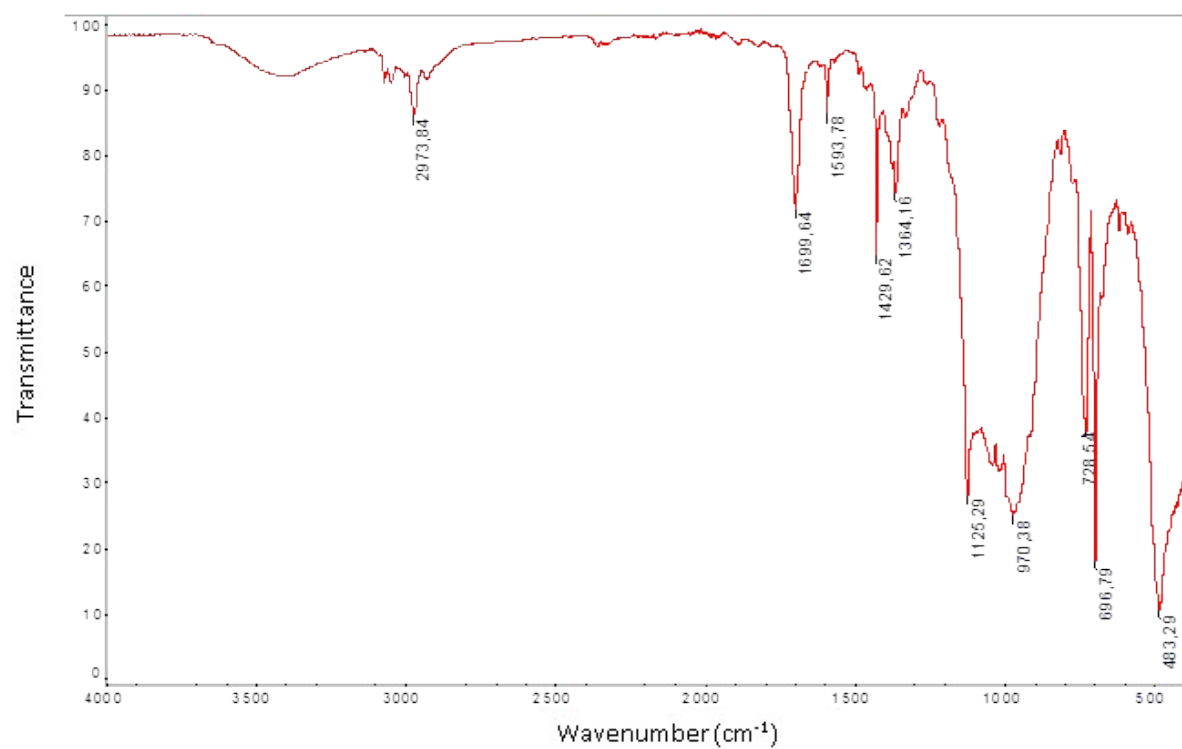


Figure S4. IR spectrum of **12**

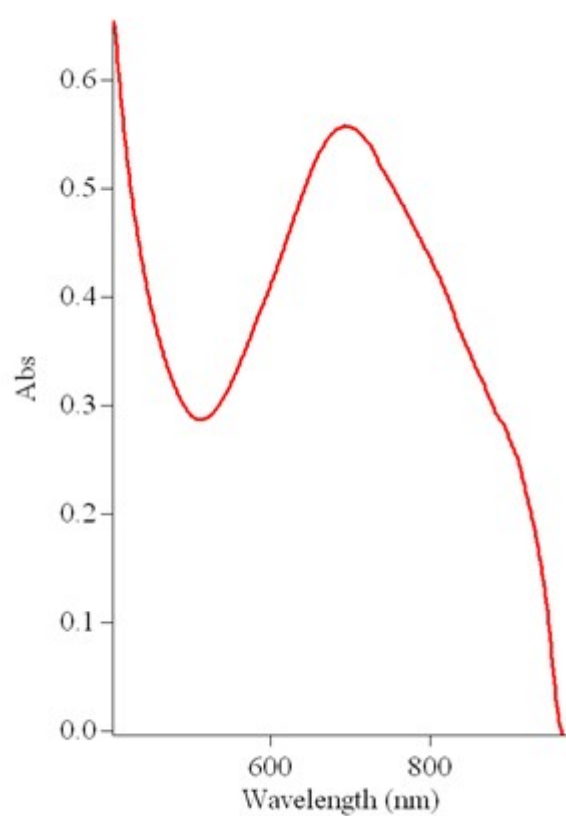
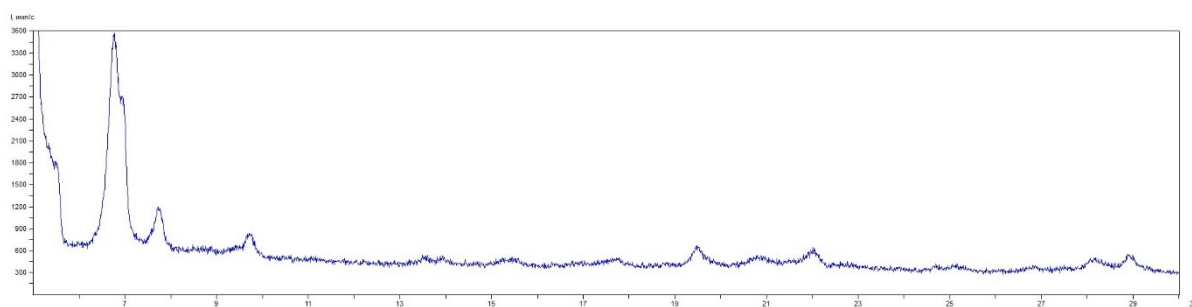
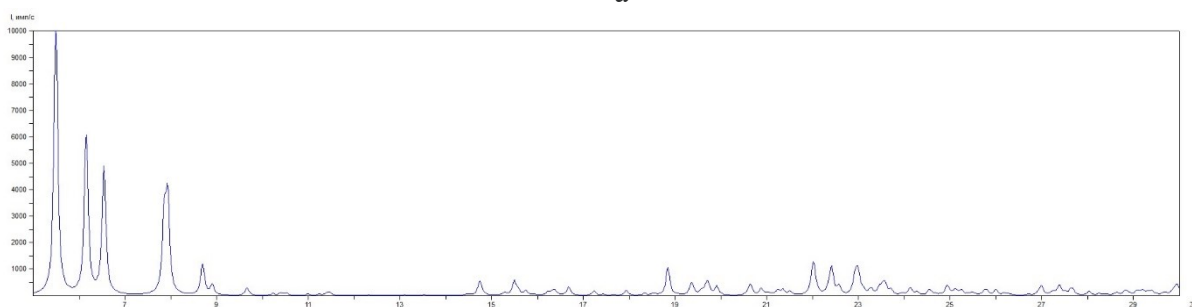


Figure S5. UV-vis spectrum of **12**



a



b

Figure S6. Powder patterns of sample **12**: experimental (top, a) and calculated (bottom, b).

Oxidation of alkanes and alcohols

Pyrex cylindrical vessels with vigorous stirring of the reaction mixture were used for the oxidation of alkanes with hydrogen peroxide. Catalytic tests were typically carried out in air in thermostated solutions. Total volume of the reaction solution was 2.5 mL (CAUTION: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). Initially, a portion of 50% aqueous solution of hydrogen peroxide was added to the solution of the catalyst and substrate in acetonitrile. The aliquots of the reaction solution were analyzed by GC (the instrument Cromas-1000, fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m \times 0.2 mm \times 0.3 μm ; helium as a carrier gas). Attribution of peaks was made by comparison with chromatograms of authentic samples, the internal standards were nitromethane for kinetic tests). Usually samples were analyzed twice, i.e. before and after the addition of the excess of solid PPh_3 . 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 PPh_3 to obtain the corresponding alcohol. This method allows us to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment. The oxidations of alcohols were carried out similarly to the procedure for the oxidation of alkanes with the addition of triphenylphosphine.

Selectivity parameters for n-heptane: C(1):C(2):C(3):C(4) = 1.0: 4.4: 4.4: 5.0, which represent 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 4 of the chain of n-heptane.

The bond-selectivity parameter for the oxidation of methylcyclohexane is $1^\circ:2^\circ:3^\circ = 1.0: 5.4: 14.8$, representing the relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of this alkane.

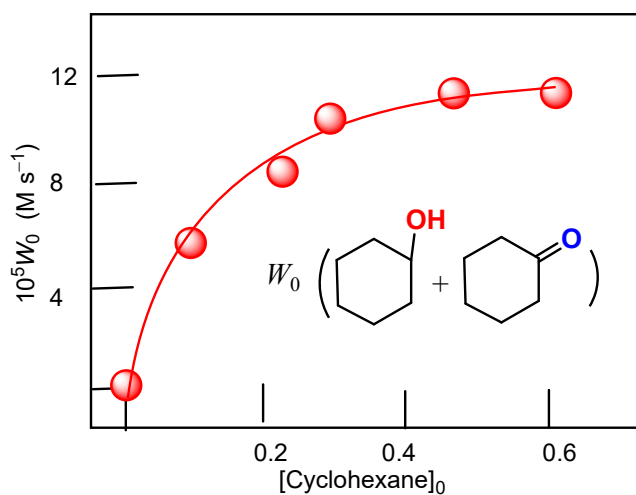


Figure S7. Dependence of the initial rate of oxygenates formation W_0 on initial concentration of cyclohexane in oxidation of cyclohexane with hydrogen peroxide (2.0 M, 50 % aqueous, 0.32ml) catalyzed by compound **12** (1×10^{-3} M, 5.2mg) in the presence of HNO_3 (0.02 M, 0.02ml stock solution 65% HNO_3 in MeCN) in MeCN (up to 2.5ml) at 60 °C. Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh_3 .

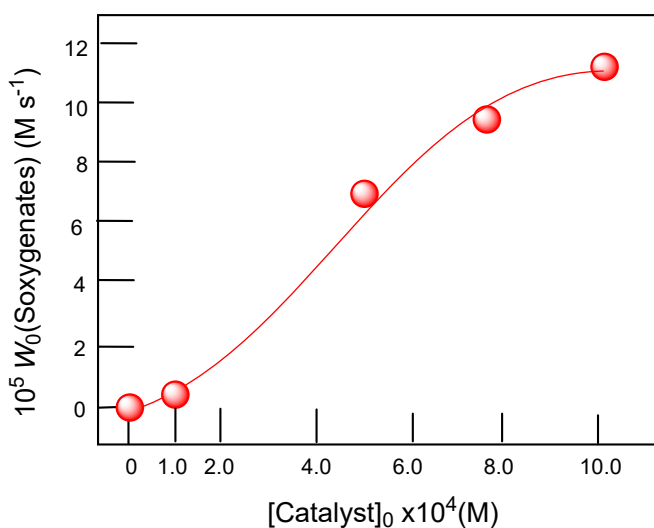


Figure S8. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 in the oxidation of cyclohexane (0.46M) with hydrogen peroxide (2.0 M, 50 % aqueous) catalyzed by compound **12** in the presence of HNO_3 (0.02 M) in MeCN up to 2.5ml, at 60° C on the initial concentration of catalyst.

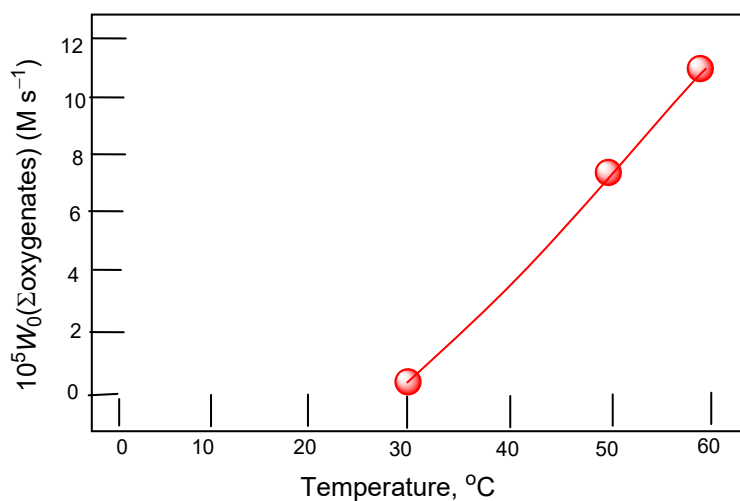


Figure S9. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 in the oxidation of cyclohexane (0.46M) with hydrogen peroxide (2.0 M, 50 % aqueous) catalyzed by compound **12** (1×10^{-3} M) in the presence of HNO_3 (0.02 M) in MeCN up to 2.5ml on reaction temperature

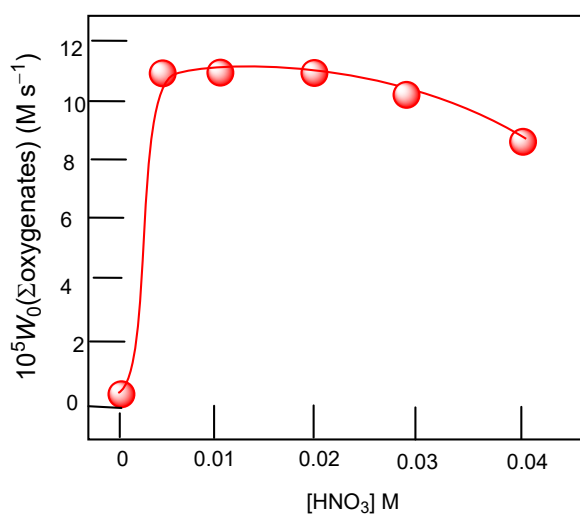


Figure S10. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 in the oxidation of cyclohexane (0.46M) with hydrogen peroxide (2M, 50 % aqueous) catalyzed by compound **12** (5×10^{-4} M) in the presence of HNO_3 in MeCN up to 2.5ml at 60° C on the initial concentration of HNO_3 .

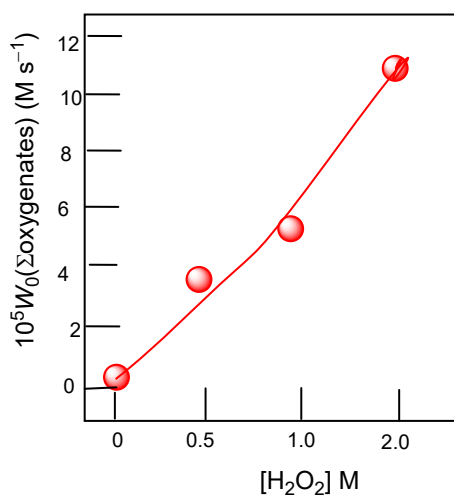


Figure S11. Dependence of the initial rate of oxygenate (sum cyclohexanol+cyclohexanone) formation W_0 in the oxidation of cyclohexane (0.46M) with hydrogen peroxide (50 % aqueous) catalyzed by compound **12** (1×10^{-3} M) in the presence of HNO_3 (0.02M) in MeCN up to 2.5ml at 60° C on the initial concentration of H_2O_2 .

Table S1. Comparison of the yields of reaction products using complex **12** and simple copper salts, as well as a blank experiment and in the absence of nitric acid

| Complex | Time (hours) of the reaction in the presence of $[\text{HNO}_3] = 2 \times 10^{-2}\text{M}$ | Total yield of oxidation products (%) | TON |
|--|---|---------------------------------------|-----|
| [12] = $1 \times 10^{-3}\text{M}$ | 2 | 28 | 129 |
| $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$ | 3 | 6 | 27 |
| $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ | 3 | 2.2 | 10 |
| No catalyst | 3 | 0 | - |
| No HNO_3 | 2 | 1.4 | 6.8 |

X-ray crystal structure determination

The single-crystal X-ray diffraction studies of **1-3**, **5-7**, **9-13** and **15-17** were carried out on a four-circle Rigaku Synergy-S diffractometer equipped with a HyPix6000HE area-detector ($T = 100$ K, $\lambda(\text{CuK}\alpha)$ -radiation, graphite monochromator, shutterless ω -scanning mode). The data were integrated and corrected for absorption by the *CrysAlisPro* program [1]. The single-crystal X-ray diffraction studies of **4**, **8** and **14** were carried out on the 'Belok/RSA' beamline ($T = 100$ K, synchrotron radiation with $\lambda = 0.79313$ Å (for **4**) or 0.74500 Å (for **8** and **14**)) of the Kurchatov Synchrotron Radiation Source using a Rayonix SX165 detector. In total, 720 frames were collected with an oscillation range of 1.0° in the φ scanning mode using two different orientations for the case of each crystal. The semi-empirical correction for absorption was applied using the *Scala* program [2]. The data were indexed and integrated using the utility *iMOSFLM* from the CCP4 software suite [3, 4]. The single-crystal X-ray diffraction study of **13a** was collected on a three-circle Bruker D8 QUEST diffractometer equipped with a PHOTON-III area-detector ($T = 100$ K, $\lambda(\text{MoK}\alpha)$ -radiation, graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program [5]. The data were indexed and integrated using the SAINT program [6]. The structures were determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms of the OH-groups and water molecules were localized in the difference-Fourier map and included in the refinement within the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the CH_3 -groups and $1.2U_{\text{eq}}(\text{C})$ for the other groups]. All calculations were carried out using the SHELXTL [7] program suite.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2355320 (**1**), CCDC 2355321 (**2**), CCDC 2355322 (**3**), CCDC 2355323 (**4**), CCDC 2355324 (**5**), CCDC 2355325 (**6**), CCDC 2355326 (**6a**), CCDC 2355327 (**7**), CCDC 2355328 (**8**), CCDC 2355329 (**9**), CCDC 2355330 (**10**), CCDC 2355331 (**11**), CCDC 2355332 (**12**), CCDC 2355333 (**13**), CCDC 2355334 (**13a**), CCDC 2355335 (**14**), CCDC 2355336 (**15**), CCDC 2355337 (**16**), and CCDC 2355338 (**17**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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