

Supplement information

for

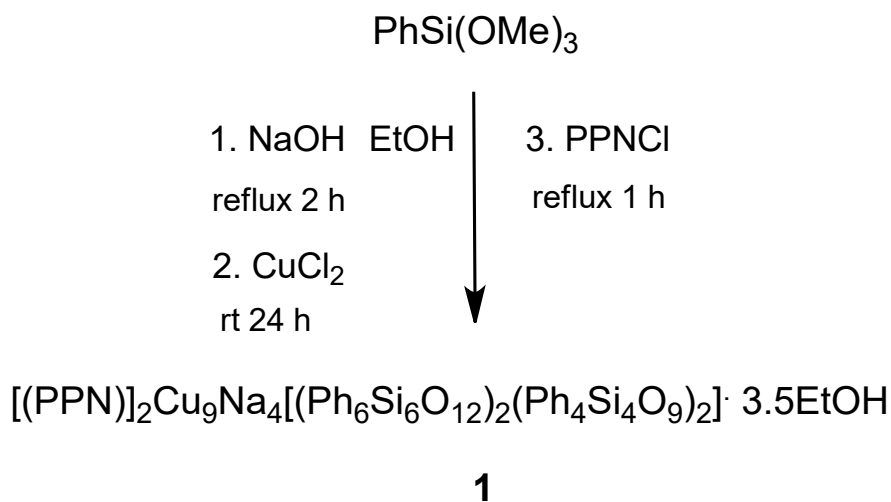
Ionic Cu₉Na₄-phenylsilsesquioxane/bis(triphenylphosphine)iminium complex: synthesis, unique structure, and catalytic activity

by

Alexey N. Bilyachenko, Victor N. Khrustalev, Zhibin Huang, Kristina D. Dubinina, Elena S. Shubina, Nikolai N. Lobanov, Di Sun, Elisabete C. B. A. Alegria, Armando J. L. Pombeiro

General Experimental Considerations

All reagents were purchased from the usual suppliers (Sigma, Fluka) and used without further purification. Elemental analysis was carried out with an XRF spectrometer VRA-30. IR spectrum of the compound (KBr pellets) was measured on a Shimadzu IR Prestige 21 FT-IR Spectrophotometer equipped with an MCT detector using a Miracle single reflection ATR unit by Pike. Set of signals: 1410–1370 cm⁻¹ (vstretchC–Si), 1110 cm⁻¹ (vasSi–O–Si), 1040 cm⁻¹ (vsSi–O–Si), 950 cm⁻¹ (vasSi–O in Si–O–M fragment), 820 cm⁻¹ and 760 cm⁻¹ (vwagC–Si). UV-Vis spectrum (10 mm optical path length, benzonitrile solution) was recorded on a Cary 50 spectrophotometer. Broad signal (peak maximum at 700 nm) points at d-d transitions. Powder pattern was measured on a Tongda TDM-20 diffractometer at room temperature (CuK α radiation, Ni filter, $\theta/2\theta$ scan from 4° to 40°)



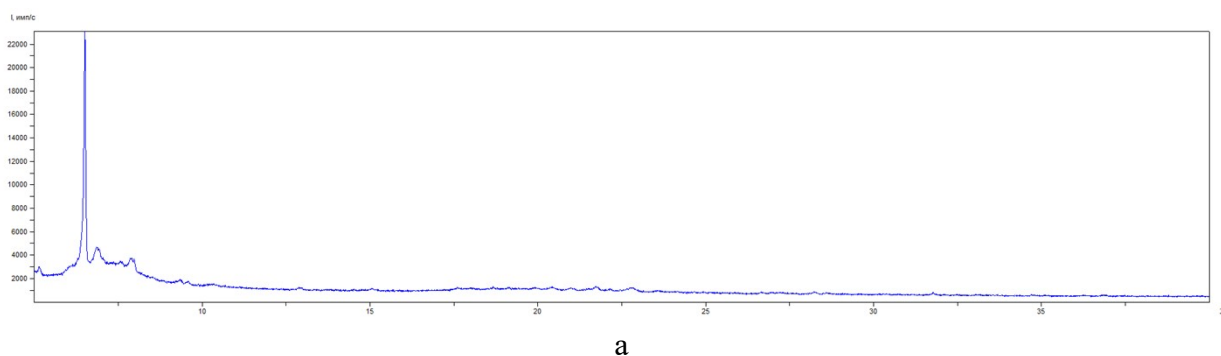
Scheme S1. General scheme of synthesis of **1**

Synthesis of **1**.

1.00 g (5.05 mmol) of $\text{PhSi}(\text{OMe})_3$ and 0.22 g (5.5 mmol) of NaOH were heated at reflux in 50 mL of ethanol for 2 h. Then, 0.30 g (2.27 mmol) of CuCl_2 was added, and the resulting mixture was stirred without heating for 24 h. Afterwards, 0.28 g (0.50 mmol) of bis(triphenylphosphine)iminium was added and the resulting mixture was heated at reflux for 1 h and then stirred without heating overnight followed by the centrifugation of precipitate. Crystallization of filtrate gave in 4-5 days a crystalline material, including single crystals that were used for X-ray diffraction analysis and powder diffraction study. The remaining part of the crystalline material was dried in vacuum to calculate yield.

Anal. Calcd for $[(\text{PPN})]_2\text{Cu}_9\text{Na}_4[(\text{Ph}_6\text{Si}_6\text{O}_{12})_2(\text{Ph}_4\text{Si}_4\text{O}_9)_2]$ Cu, 12.66; N, 0.62; Na, 2.04; P, 2.74; Si, 12.44. Found: Cu, 12.51; N, 0.57; Na, 1.95; P, 2.69; Si, 12.32. Yield: 0.78 g (69%).

Figure S1 shows powder patterns of complex **1**. Experimental (a) pattern (measured at room temperature) and calculated (from single crystal X-ray diffraction data obtained at 100 K) correspond well to each other. Small shifts of several peaks and redistribution of intensities point at some changes of cell parameters of polycrystalline sample in comparison to those of single crystal sample which could be attributed to a difference of temperatures (298 K vs 100K).



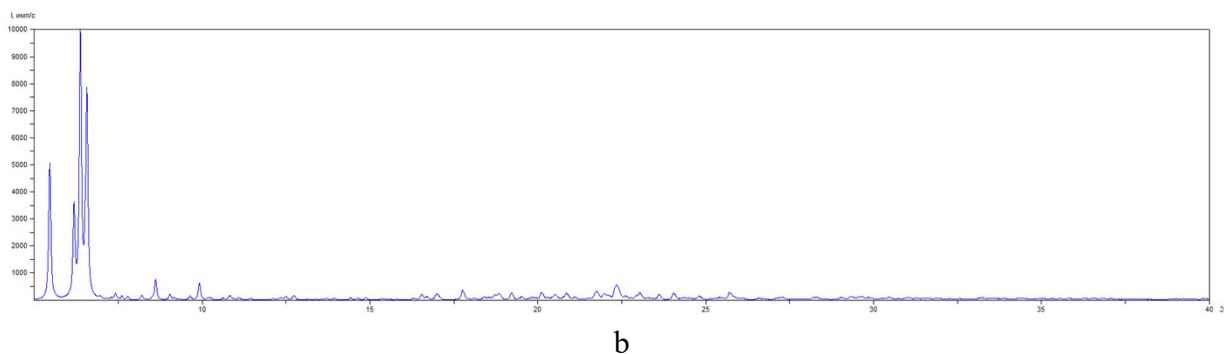


Figure S1. Powder patterns of sample **1**: experimental (top, a) and calculated (bottom, b).

Catalysis

The reactions under conventional heating (CH) were performed using a STEM heating block reactor. Each glass tube in the reactor was loaded with the catalyst (1-5 μmol), 0.5 mmol of toluene, NCMe as solvent, and 1 mmol of *tert*-butyl hydroperoxide (*t*-BuOOH, TBHP). These mixtures were then heated to 80 $^{\circ}\text{C}$ and stirred continuously at 600 rpm for a duration of up to 48 h. Upon completion, 5 μL of nitromethane (MeNO_2) were introduced as the internal standard, followed by the addition of diethyl ether to achieve a final volume of 1 mL. This allowed for the separation of the organic and aqueous phases. The organic phase was then sampled, centrifuged, and analyzed via gas chromatography. Microwave-assisted (MW) reactions were carried out using a CEM Discover instrument operating at 10 W.

The oxidation products were analysed by GC and quantified by using the internal standard method. All reaction products achieved from the catalytic oxidation reactions were identified by their retention times, confirmed with those of commercially available samples [S1-S3]. Gas chromatographic (GC) measurements were carried with an Agilent Gas Chromatograph (7820A series), equipped with a DB-624 (J&W) capillary column (DB-WAX, 30 m length, 0.32 mm internal diameter) and a FID detector. The conditions for injection included a temperature of 240 $^{\circ}\text{C}$, an initial hold at 120 $^{\circ}\text{C}$ for 1 minute, followed by a temperature ramp of 10 $^{\circ}\text{C}$ per minute up to 200 $^{\circ}\text{C}$, which was then maintained for 1 minute. Helium was used as the carrier gas throughout the process.

X-ray crystal structure determination

The single-crystal X-ray diffraction study of **1** was carried out on a three-circle Bruker D8 QUEST diffractometer equipped with a PHOTON-III area-detector ($T = 100\text{ K}$, graphite monochromator, φ - and ω -scanning mode) and corrected for absorption using the SADABS program [S4]. The data were indexed and integrated using the SAINT program [S5]. The structure was solved by intrinsic phasing modification of direct methods [S6] and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. For details, see Table 1. The hydrogen atoms of the OH-groups were localized in the difference-Fourier maps 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 the 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* program [S7].

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 2353189. 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).

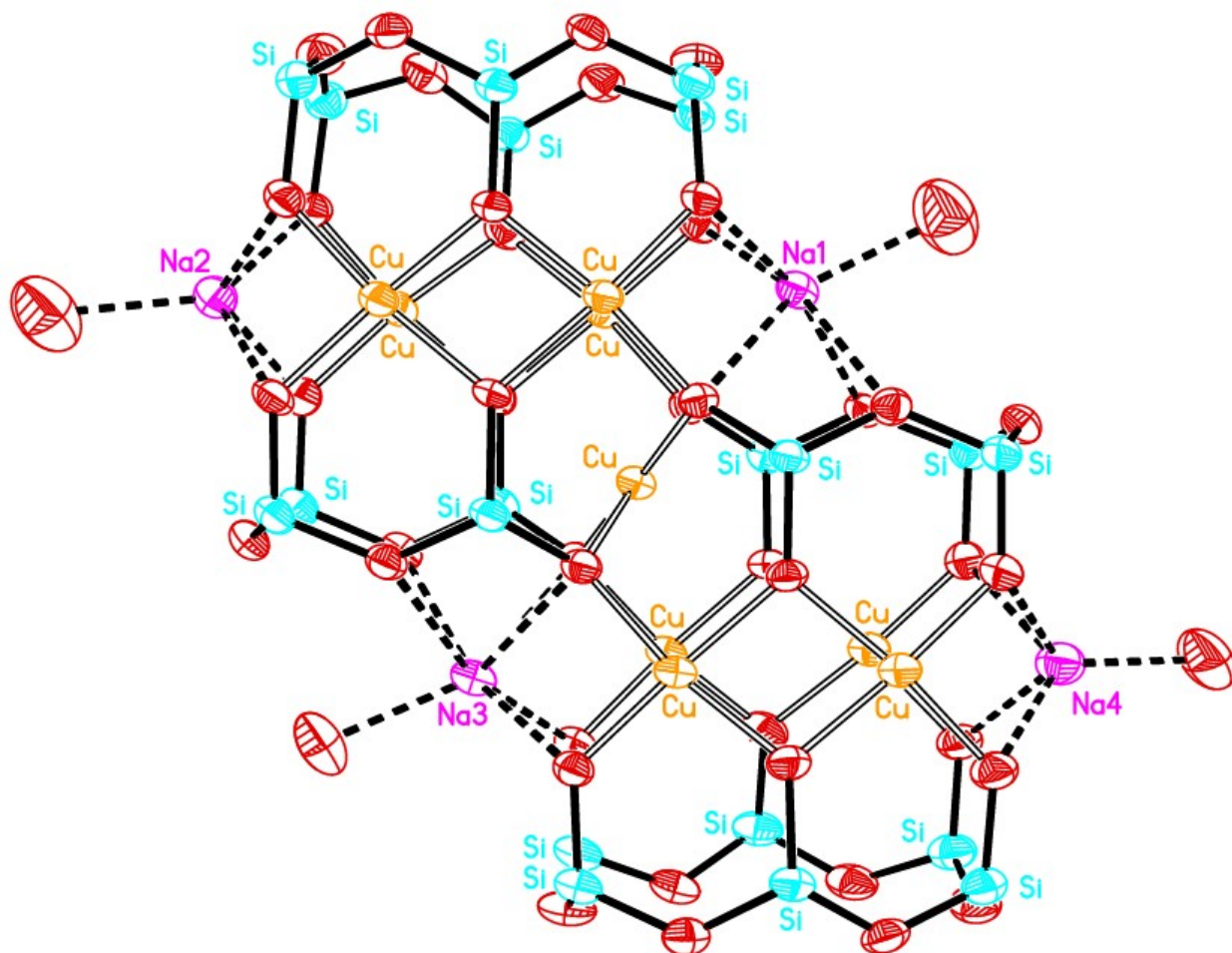


Figure S2. Molecular structure of the cage component of **1**

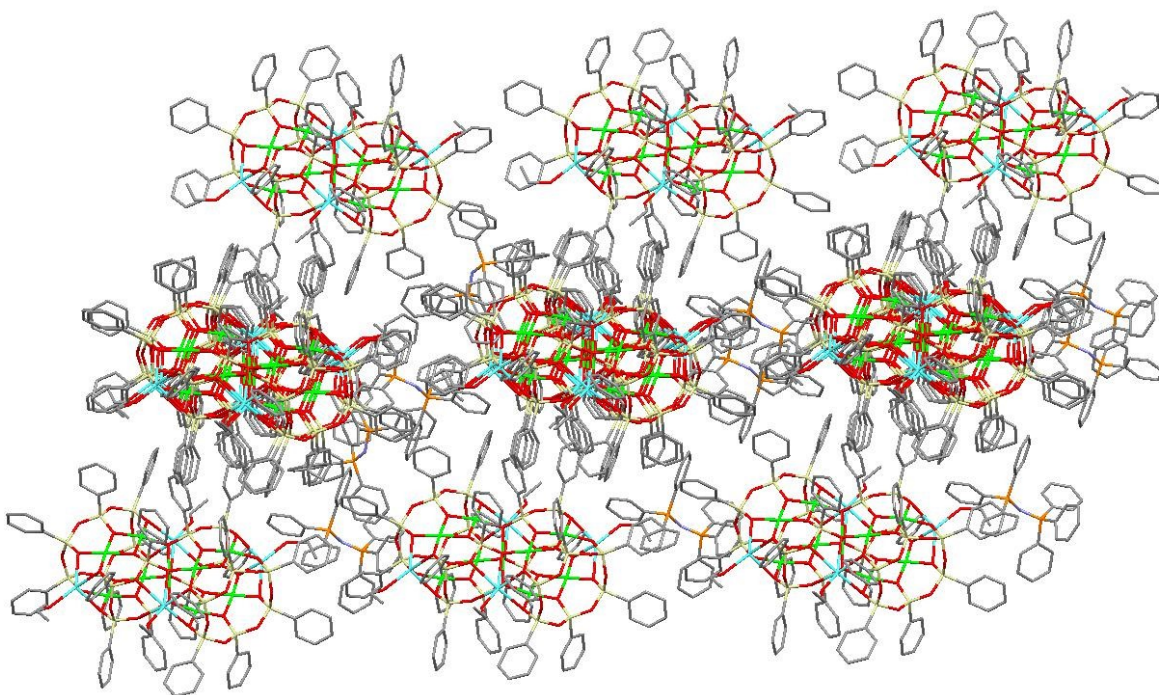
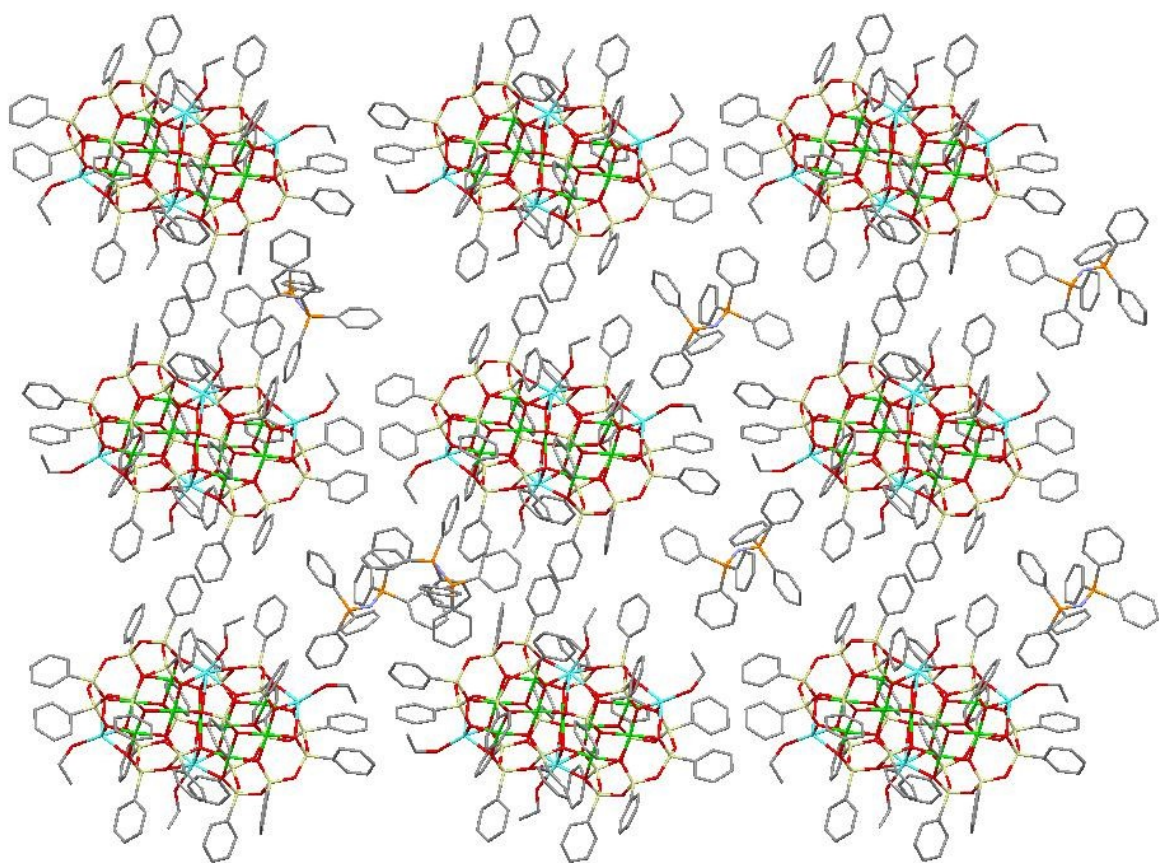


Figure S3. Two projections of crystal packing of **1**

Table 1. Crystal data and structure refinement for **1**.

Identification code	1 •3.5C ₂ H ₅ OH
Empirical formula	C ₂₀₇ H ₂₀₅ Cu ₉ N ₂ Na ₄ O _{49.5} P ₄ Si ₂₀
Formula weight	4862.33
Temperature, K	100(2)
Crystal size, mm	0.06 × 0.09 × 0.12
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , Å	16.3354(9)
<i>b</i> , Å	24.6172(13)
<i>c</i> , Å	28.7146(15)
α , deg.	75.3941(12)
β , deg.	87.8609(13)
γ , deg.	89.5919(12)
<i>V</i> , Å ³	11166.1(10)
<i>Z</i>	2
Density (calc.), Mg/m ³	1.446
μ , mm ⁻¹	1.058
<i>F</i> (000)	5004
Theta range, deg.	2.0 – 25.5
Index ranges	-19 ≤ <i>h</i> ≤ 19, -29 ≤ <i>k</i> ≤ 29, -34 ≤ <i>l</i> ≤ 34
Reflections collected	151409
Independent reflections	41427 (<i>R</i> _{int} = 0.1153)
Reflections observed	20771
<i>R</i> ₁ / w <i>R</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1034 / 0.2066
<i>R</i> ₁ / w <i>R</i> ₂ (all data)	0.1898 / 0.2383
Goodness-of-fit on <i>F</i> ²	1.059
<i>T</i> _{min} / <i>T</i> _{max}	0.876 / 0.927
$\Delta\rho_{\max}$ / $\Delta\rho_{\min}$, e·Å ⁻³	1.694 / -1.071

References

- [S1] Paul, A., Silva, T.A.R., Soliman, M.M.A., Karačić, J., Šljukić, B., Alegria, E.C.B.A., Khan, R.A., Guedes da Silva, M.F.C., Pombeiro, A.J.L., *Int. J. Hydrog. Energy*, **2022**, 47(55), 23175-23190.
- [S2] Lapa, H.M., Guedes da Silva, M.F.C., Pombeiro, A.J.L., Alegria, E.C.B.A., Martins, L.M.D.R.S. *Inorg. Chim. Acta.*, **2020**, 512, 119881.
- [S3] Sutradhar, M., Barman, T.R., Alegria, E.C.B.A., Lapa, H.M., Guedes da Silva, M.F.C., Pombeiro, A.J.L., *New J. Chem.*, **2020**, 44, 9163-9171.
- [S4] Bruker, *SAINT*, v. 8.34A, Bruker AXS Inc., Madison, WI, **2014**.
- [S5] Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., *J. Appl. Cryst.*, **2015**, 48, 3-10.
- [S6] Sheldrick, G.M. *Acta Crystallogr.* **2015**, A71, 3-8.
- [S7] Sheldrick, G.M. *Acta Crystallogr.* **2015**, C71, 3-8.