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New Cu_4Na_4- and Cu_5-Based Phenylsilsesquioxanes. Synthesis via Complexation with 1,10-Phenanthroline, Structures and High Catalytic Activity in Alkane Oxidations with Peroxides in Acetonitrile

G. S. Astakhov [1,2], M. M. Levitsky [1], A. A. Korlyukov [1,3], L. S. Shul'pina [1], E. S. Shubina [1], N. S. Ikonnikov [1], A. V. Vologzhanina [1], A. N. Bilyachenko [1,2,*], P. V. Dorovatovskii [4], Y. N. Kozlov [5,6] and G. B. Shul'pin [2,5,6,*]

1 Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ulitsa Vavilova, 28, Moscow 119991, Russia
2 Peoples' Friendship University of Russia, ulitsa Miklukho-Maklaya, 6, Moscow 117198, Russia
3 Pirogov Russian National Research Medical University, ulitsa Ostrovitianova, 1, Moscow 117997, Russia
4 National Research Center "Kurchatov Institute", pl. Akademika Kurchatova, 1, Moscow 123098, Russia
5 Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, 4, Moscow 119991, Russia
6 Chair of Chemistry and Physics, Plekhanov Russian University of Economics, Stremyannyi pereulok, 36, Moscow 117997, Russia
* Correspondence: bilyachenko@ineos.ac.ru (A.N.B.); gbsh@mail.ru or shulpin@chph.ras.ru (G.B.S.); Tel.: +7-495-135-9369 (A.N.B.); +7-495-711-8443 (G.B.S.); Fax: +7-499-135-5085 (A.N.B.); +7-495-651-2191 (G.B.S.)

Experiments

Synthesis.

$PhSi(OEt)_3$, ethanol,dimethylformamide, tetrahydrofuran and 1,10- phenanthroline were purchased from Acros Organics and used as received. All manipulations required no inert atmosphere. IR spectra for **1** and **2** were recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets. Set of signals: 1600-1400 cm-1 (νC=C, νC=N) 1120 cm^{-1} (νPh–Si), 940–1100 cm^{-1} (νasSi–O, νasSi–O–Si), 900 cm^{-1} (νasSi–O in Si–O–M fragment), 720–680 cm^{-1} (σC–H of mono-substituted phenyl group)

$PhSi(OEt)_3$ (2.0 g, 8.3 mmol), NaOH (0.33 g, 8.3 mmol), and 30 mL of an ethanol were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 2 h and then was cooled to room temperature. Then 0.37 g (2.8 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h and filtered from NaCl. The filtrate was mixed with 0.5 g (2.8 mmol) of 1,10-phenanthroline in 65 mL of THF. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. After approximately 5 days the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with n-heptane, and dried under vacuum. Dried crystalline material was used for XRF analysis (spectrometer VRA-30). Anal. Calcd for $[(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4(C_{12}H_8N_2)_4]$: Cu, 12.93; Na, 0.94; N, 3.42; Si, 13.72. Found (for vacuum-dried sample): Cu, 12.93; Na, 0.94; N, 3.42; Si, 13.72. Yield: 0.34 g (18%).

$PhSi(OEt)_3$ (1.5 g, 6.2 mmol), NaOH (0.19 g, 4.8 mmol), and 25 mL of an ethanol were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 2 h and then was cooled to room temperature. Then 0.32 g (2.4 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 3 h at 50°C and filtered from NaCl. The filtrate was mixed with 0.26g (1.4 mmol) of 1,10-phenanthroline in 55 mL of DMF. The resulting solution was intensely stirred for 2.5 h with a magnetic stirrer and then filtered from the insoluble precipitate. After approximately two weeks the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with n-heptane, and dried under vacuum. Dried crystalline material was used for XRF analysis (spectrometer VRA-30). Anal. Calcd for $[(PhSiO_{1.5})_6(PhSiO_{1.5})_7(HO_{0.5})_2(CuO)_5(O_{0.25})_2(C_{12}H_8N_2)_3]$: Cu, 12.38; N, 3.27; Si, 14.22. Found (for vacuum-dried sample): Cu, 12.31; N, 3.22; Si, 14.17. Yield: 0.34 g (28%).

Table S1. Crystallographic data for **1-2.**

datablock	**1**	**2**
Brutto formula	$C_{141.33}H_{133.67}Cu_4N_8Na_4O_{29.33}Si_{12}$	$C_{114}H_{100}Cu_5N_8O_{28}Si_{13}$
Formula weight	3096.73	2712.88
Diffractometer	MarExperts mardtb goniostat and Rayonix SX 165 detector	Bruker APEX-II CCD
Scan mode	φ scan	ω and φ scans
Anode [Wavelength, □]	synchrotron [0.986]	CuKα [1.54178]
Crystal Dimensions, mm	0.14 × 0.25 × 0.9	0.24 × 0.29 × 0.36
Crystal color	blue	blue
Crystal system	monoclinic	triclinic
a, □	23.670(5)	16.7871(3)
b, □	23.110(5)	20.6126(4)
c, □	26.970(5)	37.1418(7)
α, °	90	95.0980(10)
β, °	110.50(3)	100.7880(10)
γ, °	90	95.1000(10)

Volume, □³	13819(5)	12501.6(4)
Density, gcm⁻³	1.488	1.441
Temperature, K	100	120
T□ᵢ□/T□ₐₓ	0.51/0.74	0.5563/0.7528
μ, mm⁻◎	1.923	2.757
Space group	$P2_1/n$	$P\bar{1}$
Z	4	4
F(000)	6401	5564
Reflections collected	113928	159003
Independent reflections	15122	42922
Reflections (I>2σ(I))	12607	29146
Parameters	1544	3017
R_i□□	0.0608	0.0890
2θ□ᵢ□ - 2θ□ₐₓ, ◦	6.750 - 61.890	4.328 - 133.634
wR_2 (all reflections)	0.2397	0.1735
R_1(I>σ(I))	0.1073	0.0616
GOF	1.081	1.018
ϱ□ᵢ□/ϱ□ₐₓ, e□⁻³	-1.277/1.343	-0.629/0.994
Restraints	253	491

Single crystal X-ray studies of **2** were carried out in Center for molecule composition studies of INEOS RAS. X-ray dataset for **1** was collected in Kurchatov Centre for Synchrotron Radiation and Nanotechnology using 'Belok' beamline.

The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to

those idealized geometry and refined with constraints applied to C-H bond lengths and equivalent displacement parameters (U_{eq}(H) = 1.2U_{eq}(X), X - cental atom of XH_2 group; U_{eq}(H) = 1.5U_{eq}(Y), Y - central atom of YH_3 group. All structures were solved with the ShelXT[1] program and refined with the ShelXL[2] program. Molecular graphics was drawn using OLEX2[3] program.

CCDC 1936365-1936366 contains the supplementary crystallographic data for **1**-**2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

References:

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