



# Synthesis of functionalized silica nanostructure: Unexpected conversion of cyanopropyl group in chloropropyl one during HCl-catalysed hydrolysis of the corresponding triethoxysilane

Ana–Maria-Corina Dumitriu, Mihaela Balan, Alexandra Bargan, Sergiu Shova, Cristian-Dragos Varganici, Maria Cazacu\*

*“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi, 700487, Romania*

## ARTICLE INFO

### Article history:

Received 20 October 2015

Received in revised form

17 January 2016

Accepted 18 January 2016

Available online 21 January 2016

### Keywords:

Cubic polyhedral silsesquioxanes

Synthesis

Structural characterization

Functionalized silica

Nanosized structures

## ABSTRACT

During acid hydrolysis of 3-cyanopropyltriethoxysilane (CyTES) in a molar ratio HCl: CyTES – 4.6:1 in methanol, with the intention to prepare the properly polyhedral oligomeric silsesquioxane (POSSQ) or carboxyl derivative, the conversion of organic functional group occurred by replacing the CN group with Cl forming octakis(chloropropyl)octasilsesquioxane (Cl-POSSQ). The structure was determined through X-ray single crystal diffraction, spectral (FTIR and NMR) techniques and elemental analysis. The stepwise conversion of the CN group during the 3-cyanopropyltriethoxysilane hydrolysis was monitored through IR and  $^{13}\text{C}$  NMR spectroscopy. Thermal behavior was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Moisture sorption capacity was evaluated by water vapor sorption in dynamic regime (DVS). The biological activity was *in vitro* tested against three fungi and two bacteria.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Polyhedral oligosilsesquioxanes are hybrid organic-inorganic architectures with well-defined and highly symmetrical structures. These consist in an inner inorganic frameworks formed by alternating silicon and oxygen atoms surrounded by H or organic substituents (a wide range of alkyl, alkenyl, aryl, or siloxy groups) in three dimensional arrangements [1–3]. Their properties are combinations of those of the two components, making them really nanocomposite materials [2,4–6]. The most representative members of this family are the cubic ( $n = 8$ ),  $\text{R}_8\text{Si}_8\text{O}_{12}$  or  $\text{T}_8$ , whose formation is favored by the steric effects [3,7,8].

The main ways for the synthesis of  $\text{T}_8$  cores are the acid or base catalysed hydrolytic polycondensation of simple chloro- or alkoxy-silanes and hydroxide/fluoride catalysed rearrangement of silsesquioxane resins [5,9,10]. Although seemingly simple, the procedure for the preparation of the silsesquioxanes by hydrolytic condensation reactions of  $\text{RSiX}_3$  is a complex, multistep, time-consuming process. These processes are influenced by reaction

conditions such as reagent concentration, solvent, nature of R and X groups, catalyst type, water addition, and solubility of the condensation products [2,4,10,11]. A high number of intermediates are formed, all in equilibrium with one another. However, by choosing appropriate conditions, the reaction can be directed mainly towards obtaining the desired compound, some rules in this regard already being outlined. Thus, high concentrations of silane monomer, high pH and polar solvents favor the formation of silsesquioxane polymers, while high dilution, low pH and inert organic non-polar solvents favor intramolecular condensation mainly cyclization occurs yielding polyhedral silsesquioxanes. More reactive R and X groups, such as R = hydrogen, methyl and X = Cl, OH, undergo faster hydrolysis and favor the formation of silsesquioxane polymers. Water is needed to achieve hydrolysis and cyclization, but too much water in the reaction causes polymer formation. The solubility of a specific silsesquioxane species formed during the condensation reaction, which in part is dictated by the type of R group on the monomer, has a large influence over the yield of that species. The less soluble species precipitates from the reaction medium thus pushing the equilibrium towards the formation of that species [2,4,10,11]. In this paper we report the acid hydrolysis of a trialkoxysilane having reactive organic group attached to the silicon atom, 3-cyanopropyltriethoxysilane, in

\* Corresponding author.

E-mail address: [mcazacu@icmpp.ro](mailto:mcazacu@icmpp.ro) (M. Cazacu).

presence of a high excess of HCl (alkoxysilane:HCl molar volume 1:4.64) and at high dilution in methanol (reactants mass: solvent volume around 1:10). The separated product was structurally characterized. Its thermal and moisture behaviors were also studied.

## 2. Experimental section

### 2.1. Materials

3-Cyanopropyltriethoxysilane (98%,  $d_{20}^{\circ\text{C}} = 0.966$  g/mL), and hydrochloric acid ( $c = 37\%$ ) were purchased from Sigma Aldrich and used as such. Methanol p.a. was acquired from Chemical Company.

### 2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. Analyses were performed in the transmission mode in the 400–4000  $\text{cm}^{-1}$  range, at room temperature, with a resolution of 2  $\text{cm}^{-1}$  and accumulation of 32 scans. The samples were incorporated in dry KBr and processed as pellets in order to be analyzed.

The NMR spectra were recorded on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and z-gradients. Spectra were recorded in DMSO- $d_6$ , at room temperature. The chemical shifts are reported as  $\delta$  values (ppm) relative to the solvent residual peak.

The carbon, hydrogen, and nitrogen contents were determined by standard methods.

The thermogravimetric analyses were performed on STA 449F1 Jupiter NETZSCH (Germany) equipment. The measurements were made in the temperature range 30–700 °C under a nitrogen flow (50 mL/min) using a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were conducted on a DSC 200 F3 Maia device (Netzsch, Germany) at a heating and cooling rate of 10 °C  $\text{min}^{-1}$  in nitrogen atmosphere at a flow rate of 50  $\text{mL min}^{-1}$ .

Dynamic water vapor sorption (DVS) capacity of the samples was determined in the relative humidity (RH) range 0–90% by using the fully automated gravimetric analyzer IGAorp produced by Hidden Analytical, Warrington (UK).

### 2.3. X-ray crystallography

Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation. The crystal was placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [12]. The structure was solved by direct methods using Olex2 [13] software with the SHELXS [14] structure solution program and refined by full-matrix least-squares on  $F_0^2$  with SHELXL-97 [14]. Atomic displacements for non-hydrogen, non-disordered atoms were refined using an anisotropic model. Three of eight 3-chloropropyl fragment in structure **Cl-POSSQ** presented too large thermal ellipsoids, so that disordered models, in combination with the available tools (PART, DFIX, and SADI) of SHELXL97 were applied in order to better fit the electron density. The combined anisotropic/isotropic refinement has been used for these non-H atoms. The main crystallographic data together with refinement details are summarized in Table 1, while the selected bond lengths and angles in Table 1S.

CCDC-959468 (**Cl-POSSQ**) contains the supplementary crystallographic data for this contribution (Table 3). This data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving](http://www.ccdc.cam.ac.uk/conts/retrieving).

**Table 1**

Crystallographic data, details of data collection and structure refinement parameters for the compound **Cl-POSSQ**.

	Cl-POSSQ
Empirical formula	$\text{C}_{24}\text{H}_{48}\text{Cl}_8\text{O}_{12}\text{Si}_8$
Formula weight	1036.94
Temperature/K	200
Crystal system	triclinic
Space group	$P-1$
$a/\text{\AA}$	10.1724(10)
$b/\text{\AA}$	15.1986(15)
$c/\text{\AA}$	15.7965(13)
$\alpha/^\circ$	99.657(7)
$\beta/^\circ$	104.169(8)
$\gamma/^\circ$	98.317(8)
$V/\text{\AA}^3$	2289.9(4)
$Z$	2
$D_{\text{calc}}/\text{mg}/\text{mm}^3$	1.504
$\mu/\text{mm}^{-1}$	0.751
Crystal size/ $\text{mm}^3$	$0.10 \times 0.10 \times 0.20$
$\theta_{\text{min}}, \theta_{\text{max}}/^\circ$	3.44 to 52
Reflections collected	17034
Independent reflections	8966 [ $R_{\text{int}} = 0.0405$ ]
Data/restraints/parameters	8966/8/469
$R_1^a(I > 2\sigma(I))$	1.028
$wR_2^b(\text{all data})$	0.0968
GOF $^c$	0.2601
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}/e/\text{\AA}^3$	0.92/−0.83

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

<sup>c</sup>  $\text{GOF} = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where  $n$  is the number of reflections and  $p$  is the total number of parameters refined.

[html](#) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### 2.4. Procedure

8.779 g (0.038 mol) 3-cyanopropyltriethoxysilane, 250 mL methanol and 15 mL hydrochloric acid 37% were introduced in a well dried round bottom flask, in nitrogen atmosphere. The mixture was stirred 1 h and then left to rest at room temperature. Colorless crystals, suitable for XRD were formed after ten weeks from solution (yield: 1.45 g, 29.50%). Elemental analysis, % wt: Found: C, 26.79; H, 4.50; Calculated for the molecular formulae  $\text{C}_{24}\text{H}_{48}\text{Cl}_8\text{O}_{12}\text{Si}_8$  ( $M = 1073$  g/mol): C, 26.84; H, 4.47. IR (KBr pellet,  $\text{cm}^{-1}$ ): 403w, 478m, 536w, 553w, 648w, 698m, 798m, 868m, 910w, 964w, 1007m, 1047s, 1111vs, 1190m, 1242w, 1271m, 1313w, 1350vw, 1410w, 1441w, 1458 w, 2957m (Fig. 1S).  $^1\text{H-NMR}$  (400.13 MHz, DMSO- $d_6$ ): 0.79 (pen,  $J = 4$  Hz, Si- $\text{CH}_2$ -), 1.80 (pen,  $J = 7.3$  Hz, Si- $\text{CH}_2$ - $\text{CH}_2$ -), 3.62 (t,  $J = 6.6$  Hz, Si- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -Cl), intensities ratio: 1:1:1 (Fig. 3S).  $^{13}\text{C-NMR}$  (100.6 MHz, DMSO- $d_6$ ): 8.66 (Si- $\text{CH}_2$ -), 25.86 (Si- $\text{CH}_2$ - $\text{CH}_2$ -), 47.14 (Si- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -Cl).  $^{29}\text{Si-NMR}$  (79.49 MHz, DMSO- $d_6$ ): −66.54 (Fig. 4S).

## 3. Results and discussion

3-cyanopropyltriethoxysilane, CyPTES was treated with a high excess of concentrated aqueous solution of HCl (37 wt%) (molar ratio CyPTES:HCl = 1:4.6) for the purpose of its hydrolysis and further condensation leading to proper octahedral silsesquioxane, according to the well-known general procedure [3].

The reaction consisted of mixing the reactants at room temperature, stirring for 1 h and then keeping the reaction mixture in static regime until this became heterogeneous by the formation of a crystalline phase. After isolation, this phase was analyzed further. A

Download English Version:

<https://daneshyari.com/en/article/1405076>

Download Persian Version:

<https://daneshyari.com/article/1405076>

[Daneshyari.com](https://daneshyari.com)