# SYNTHESIS AND CHARACTERIZATION OF OCTAKIS(3-CHLOROAMMONIUMPROPYL)OCTASILSESQUIOXANE

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The acid hydrolysis of 3-aminopropyltriethoxysilane afforded a cubic octakis(3-chloroammoniumpropyl)octasilsesquioxane (**1**). The compound prepared was characterized by elemental analysis and spectroscopic methods (IR, and NMR). X-ray single crystal diffraction revealed the inner and outer diameters of the nanostructure are of 0.53 and 1.70 nm, respectively. Thermal and moisture behaviours were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and water vapour sorption in dynamic regime (DVS), respectively. Biological activity was also tested.
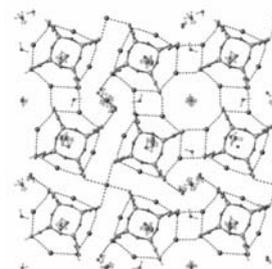
INTRODUCTION

Polyhedral oligosilsesquioxanes (POSSs) with the general formula $Si_nO_{3n/2}R_n$ or T_nR_n (where n=4, 6, 8, 10, 12, and R=H, or a wide range of alkyl, alkenyl, aryl, or siloxy groups, and their organofunctional derivatives) are a group of organosilicon compounds with well-defined and highly symmetrical structures.[1-3] The leading representatives are the completely condensed structures with eight silicon atoms, cubic, $R_8Si_8O_{12}$ or T_8, whose formation is favoured by the steric effects.[3-5] These compounds are organic-inorganic architectures, with inner inorganic frameworks consisting of silicon and oxygen atoms surrounded by organic R substituents, in three-dimensional arrangements.[1-3] Recent studies revealed that the silsesquioxane cage appears to be involved in electron delocalization with attached conjugated organic.[2] In fact, the organic group, R, determines many of the physical and chemical properties of the cage molecule.[1] Depending on the reactivity of the organic group R, POSSs can be classified as nonfunctional and functional. The reactive R groups permit the chemical bonding of the cages to different substrates.[3] These compounds have been used as "nanobuilding blocks" for polymer networks, as filler for nanocomposites, as cores for dendrimers, flow aids for high temperature thermoplastics, etc.[6-8] Some promising bio-inspired

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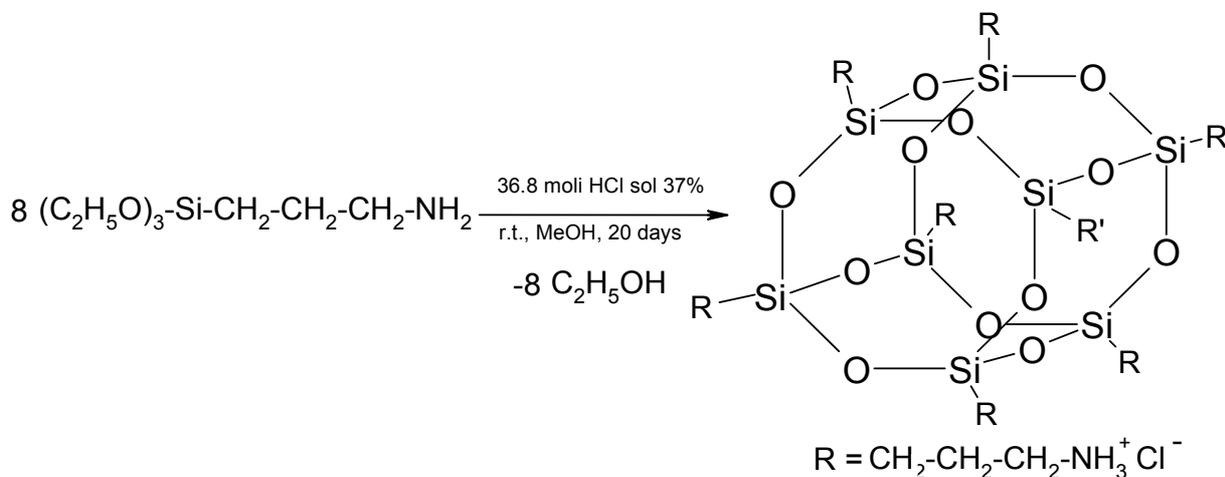research areas for POSS include bone growth and soft tissue healing.[8]

In this paper we report the synthesis, structural data and some properties for the acid hydrolysis product of 3-aminopropyltriethoxysilane, this being octakis(3-chloroammoniumpropyl)octasilsesquiox-ane (**1**). The hydrolytic condensation of 3-aminopropyltriethoxysilane catalysed by quaternary ammonium bases[3,9] or by hydrochloride acid[6,10-15] has been reported. It is to note that in the last case the reaction mainly resulted with the formation of chlorohydrate derivative.[13-15] Unfortunately, neutralization of the hydrochloride to free amine is difficult to achieve without affecting the Si-O bond. However, both forms (amine and its hydrochloride salt) allow obtaining a wide range of functionalized silsesquioxanes.[16] In literature is reported the solid state structure of octakis(3-chloroammoniumpro-pyl)octasilsesquioxane established by X-ray single crystal diffraction in form of the mixed tetrachlorozinc and chloride salt.[7] Here, it is for the first time when the structure of this compound as such was established, and the role of the hydrogen bonds in the crystal structure formation is discussed. Thermal and moisture behaviour as well as biological activity of this compound were studied.

RESULTS AND DISCUSSION

The main ways for the synthesis of T_8 cores are the acid or base catalysed hydrolytic polycondensation of chloro- or alkoxysilanes and hydroxide/fluoride catalyzed rearrangement of silsesquioxane resins.[17-19] In our approach, 3-aminopropyltriethoxysilane as a solution diluted with methanol was treated with HCl in very high excess at room temperature under stirring according to procedure described by Feher,[16] the most used synthetic route to oligosilsesquioxanes and their homo derivatives.[3] In these conditions, the hydrolysis of trialkoxysilane and subsequent condensation occur with formation of corresponding silsesquioxane (Scheme 1) separated from the reaction mixture, after a long period of time, as colorless crystals.

The elemental analysis values for the compound correspond to the closed cubes, with amine functional groups in chlorohydrate form. This composition is confirmed by single crystal X-ray diffraction. In FTIR spectrum of compound **1**, the v_{as}(Si-O-Si) is assigned as occurring at 1109 cm^{-1} close to values reported in literature[17,20,21] for $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$. The band at 1579 cm^{-1} belongs to N-H bond, while that around 3436 cm^{-1} indicates the presence of the water molecules in compound. ^{1}H NMR spectrum shows peaks at chemical shifts and intensity corresponding with the proposed structure. The peaks for the four proton types from $\equiv$Si-CH$_2$-CH$_2$-CH$_2$-NH$_3^+$Cl$^-$ group can be seen at 0.725-0.766, 1.704-1.784, 2.771-2.809 and 8.258 ppm, respectively in intensity ratio: 1:1:1:1.5 (Fig. 1). In ^{29}Si NMR, the peak at 66.49 ppm is characteristic for silicon from a cubic architecture (Fig. 2).

$$8 \ (C_2H_5O)_3\text{-Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 \xrightarrow[\text{r.t., MeOH, 20 days}]{\text{36.8 moli HCl sol 37\%}}$$

$$-8 \ C_2H_5OH$$

$$R = CH_2\text{-CH}_2\text{-CH}_2\text{-NH}_3^+ \ Cl^-$$

Scheme 1 – Hydrolysis reaction leading to octasilsesquioxane **1**.
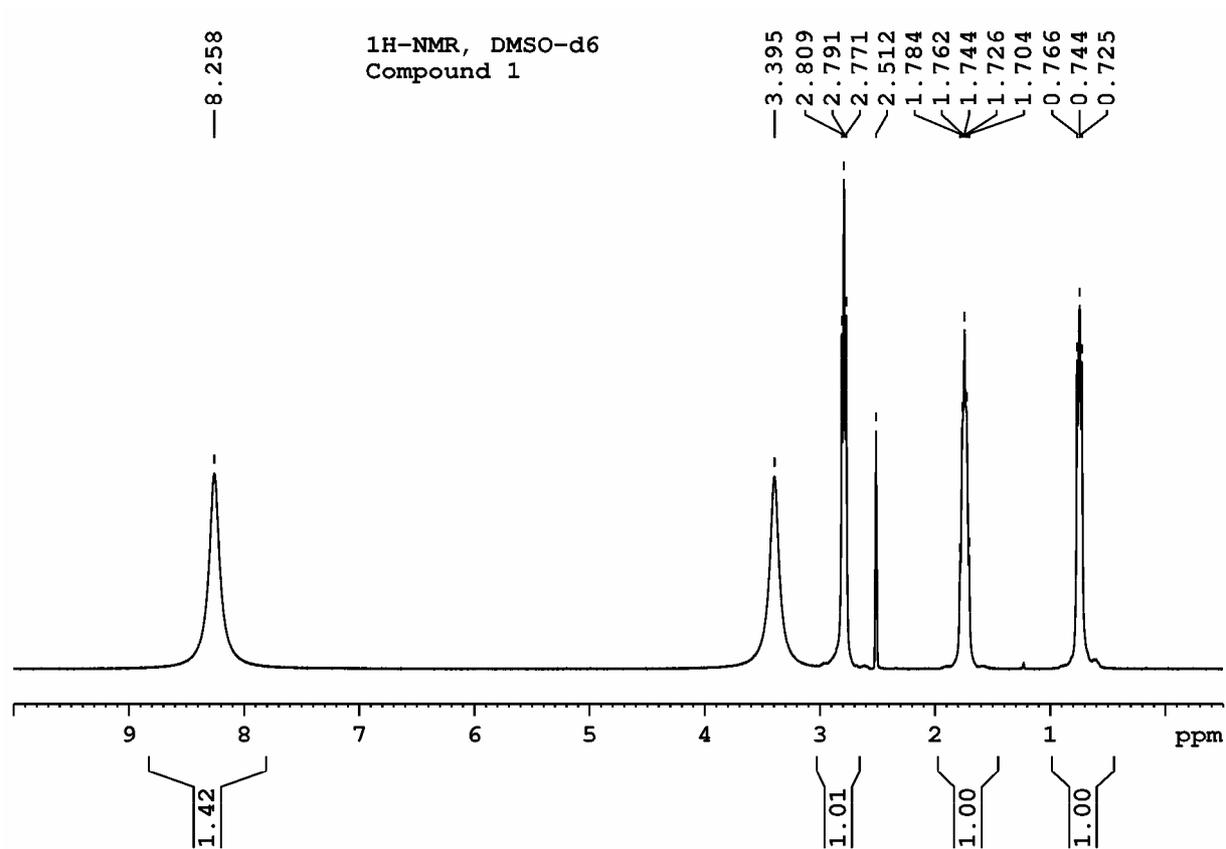
Fig. 1 – ^{1}H NMR spectrum for the compound **1**.
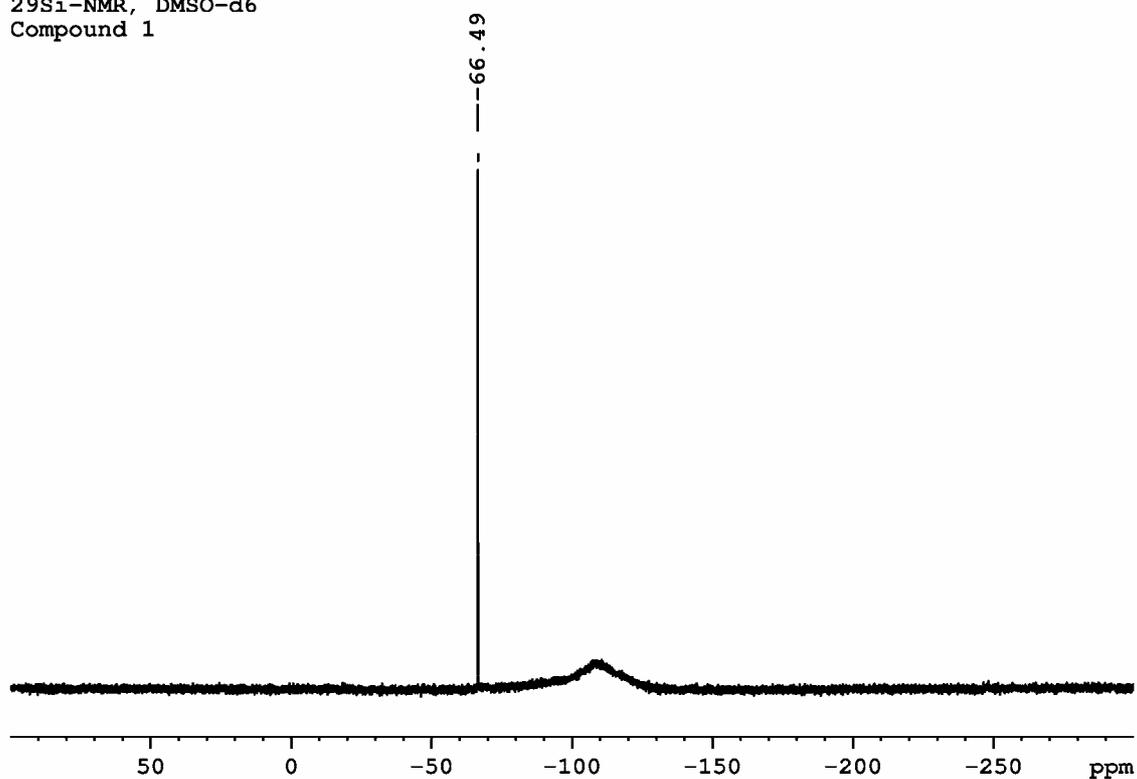
Fig. 2 – ^{29}Si NMR Spectrum of compound **1**.

Crystal structure analysis

According to the X-ray crystallography, compound **1** presents an ionic crystal structure built from octakis(3-ammoniumpropyl)octasilsesquioxane cations, chloride anions and solvate water molecules. The final composition of this compound is in agreement with an average formula of $[ClH_3N(CH_2)_3]_8Si_8O_{12}$ $4.2H_2O$. The silsesquioxane octa-cation exhibits the own symmetry since the oxygen atoms O5, O6, O7 and O8 occupy the special position on the crystallographic plane *m*. As mentioned above, the structure of $[H_3N^+(CH_2)_3]_8Si_8O_{12}$ cation has been reported earlier[6] as a non-stoichiometric mixture of Cl⁻ and $[ZnCl_4]^{2-}$ salt. The crystal structure of compound **1** is characterized by a large disorder for the positions of the amine side-arms, as well as for the both anions, so that the role of the hydrogen bond in the crystal structure formation was not discussed. Four chloride anions are also disordered within five partially occupied crystallographic positions. This is presumably due to the packing features which aim to provide condition for the all possible intra- and intermolecular H-bond formation with NH_3^+ as donor (Fig. 3).

The characteristics of hydrogen bond are presented in Table 1. It is important to note that the eight 3-aminopropyl arms in compound **1** adopt the same "squashed" conformation (Fig. 3b) as observed in ref.[6] for $\{[H_3N(CH_2)_3]_8Si_8O_{12}\}[ZnCl_4]$ $2\cdot4Cl$.

However, in compound **1** the Si_8O_{12} cube exhibits less elongation along the direction that the eight 3-aminopropyl arms are squashed, since the Si1•••Si4 3.1405(5) Å and Si2•••Si3 3.129(6) Å lie in the narrow range with that of Si1•••Si1i 3.092(5) Å, Si2•••Si2i 3.116(6) Å, Si3•••Si3i 3.110(5) Å and Si4•••Si4i 3.091(5) Å (Fig. 3b). This conclusion is confirmed also by the analysis of Si1-O-Si4 152.1(5)° and Si2-O3-Si2 148.2(5)° with those associated with the elongation Si1-O5-Si1i, S2-O6-Si2i, Si3-O7-Si3i and Si4-O8-Si4i in the range between 145.7(6) and 150.4(8)°.

The components of the structure are arranged in the crystal space into two-dimensional layers (Fig. 4) due to the multiple intermolecular N-H⋯Cl, N-H⋯O and C-H⋯Cl interactions. These 2D layers are further weakly interacting through the N-H⋯O, O-H⋯O and C-H⋯Cl hydrogen bonds involving solvate water molecules. The shortest Si_8O_{12} centroid-to-centroid separation is equal to 9.559 Å. As a whole, the crystal structure can be characterized as a complex three-dimensional supramolecular architecture containing large channels occupied by statistically distributed water molecules, the positions of which are not fully occupied. The solvent accessible volume calculated using corresponding subroutine of Olex2 constitutes 33.8 %. O⋯O distance within the cage (inner diameter) and N⋯N distance (outer diameter) in cubic polyhedral structure, estimated on the basis of the crystallographic data, were: 0.53 and 1.70 nm, respectively.

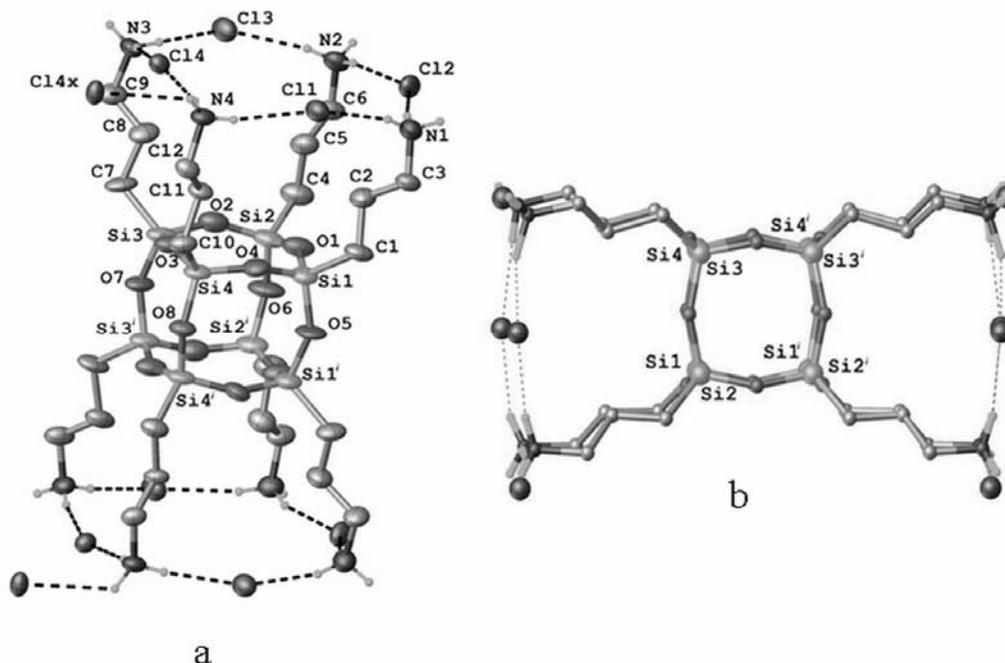Fig. 3 – a – X-ray structure of $[ClH_3N(CH_2)_3]_8Si_8O_{12}$ unit in the crystal structure **1**. Thermal ellipsoids are drawn at 30% probability level. Non-relevant hydrogen atoms are not shown for clarity. All the anion sites are partially occupied; b – The squashed orientation of the 3-aminopropyl arms in **1**. Symmetry code: i) x, y, 1-z.

Table 1

H-bonds parameters

| D-H···A	Distance, Å			Angle D-H···A, deg	Symmetry code
	D-H	**H···A**	**D···A**		
[ClH$_3$N(CH$_2$)$_3$]$_8$Si$_8$O$_{12}$ 4.2H$_2$O (1)					
N1-H···Cl1	**0.89**	**2.31**	**3.145(8)**	**156.9**	*x, y, z*
N1-H···Cl2	0.89	2.36	3.220(9)	162.6	*x, y, z*
N1-H···Cl3	0.89	2.36	3.185(8)	153.9	Y, 1-x, z
N2-H···Cl2	0.89	2.30	3.166(8)	163.0	*x, y, z*
N2-H···Cl2	0.89	2.37	3.136(8)	144.5	1-y,x,z
N2-H···Cl3	0.89	2.33	3.207(9)	167.8	*x, y, z*
N3-H···Cl3	0.89	2.32	3.189(8)	166.2	*x, y, z*
N3-H···Cl4	0.89	2.33	3.185(8)	162.5	*x, y, z*
N3-H···Cl1	0.89	2.79	3.260(8)	114.0	1+y, 1-x, z
N3-H···O2*w*	0.89	2.66	3.509(8)	160.5	1+y, 1-x, z
N4-H···Cl1	0.89	2.34	3.229(8)	169.6	*x, y, z*
N4-H···Cl4x	0.89	2.90	3.396(8)	116.4	*x, y, z*
N4-H···Cl4	0.89	2.28	3.166(1)	162.3	*x, y, z*

a

b
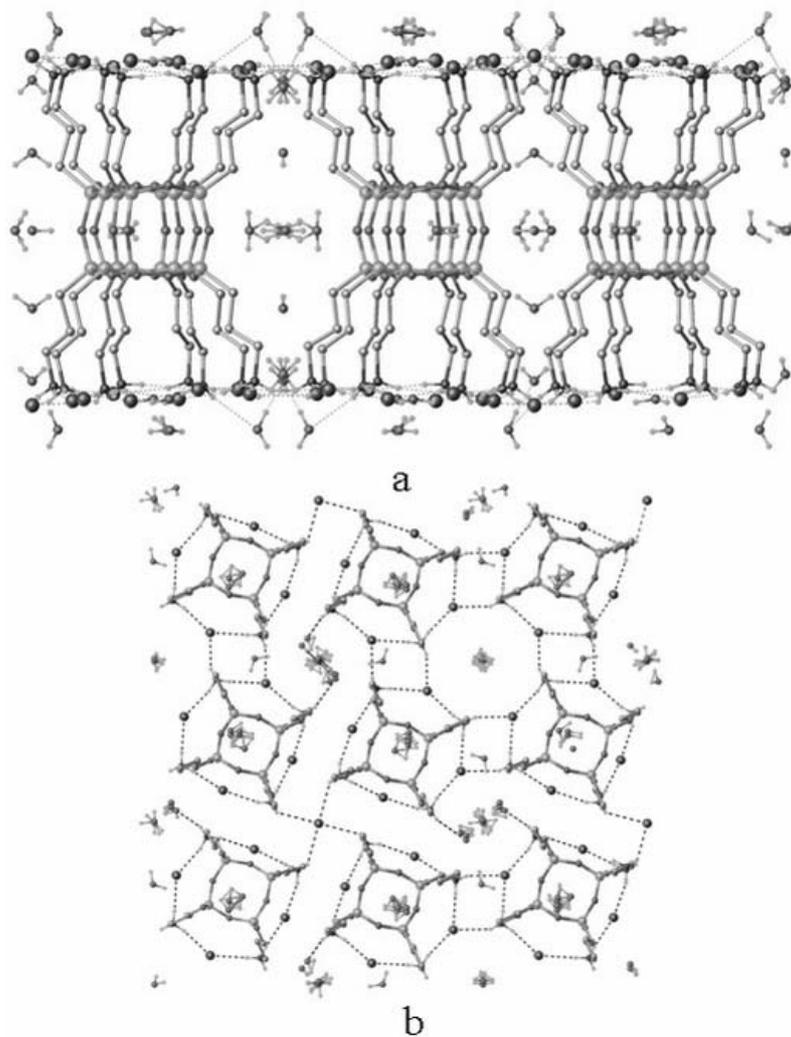
Fig. 4 – a – The view of two-dimensional supramolecular layer along *b* crystallographic axis in the crystal structure **1;** b – The view of two-dimensional supramolecular layer along *c* crystallographic axis in the crystal structure **1** (color codes: Si – orange, Cl – green; O – red, C – grey, H – blue).

The thermal behaviour

The thermal stability of the POSSs is closely dependent on the nature of the organic group attached to the silicon atom. In our case, the compound contains the nucleophilic ($-NH_3^+Cl^-$) group which, particularly at higher temperatures, contributes to the breaking of siloxane bonds.[1] As a result, the sample **1** breaks down suddenly, almost completely, in a single step starting from 243 °C, leaving a residue of only 5 wt% (Fig. 5a, Table 2). Very weak transitions are visible on the DSC curves at -6 °C on the second heating curve and at -11 °C on the cooling curve, corresponding to melting and crystallization, respectively (Fig. 5b).

The moisture stability of the isolated compound was evaluated by water vapour sorption analysis in dynamic regime. Sorption-desorption isotherms were registered at three temperatures: 25°C, 35°C and 55°C (Fig. 6). As can be seen, the sample **1** shows similar isotherms at the three studied temperatures having hysteresis on the entire approached humidity range; however, the hystereses are higher at increased humidity. The maximum water vapour sorption capacity at highest humidity increases as the temperature rises from 17.3 wt% at 25 °C at 27.3 wt% at 35 °C and 41.1 wt% at 55 °C. The sample retains small amounts of water (between 0-5 wt%) after desorption, at all temperatures, which likely remains in free positions of wide channels of the crystal structure.

The biological tests showed the compound **1** had no effect against tested fungi (*Aspergillus niger, Penicillium frequentans, Alternaria alternata*) and both Gram-negative (*Pseudomonas aeruginosa*) and Gram-positive (*Bacillus polymyxa*) bacteria.
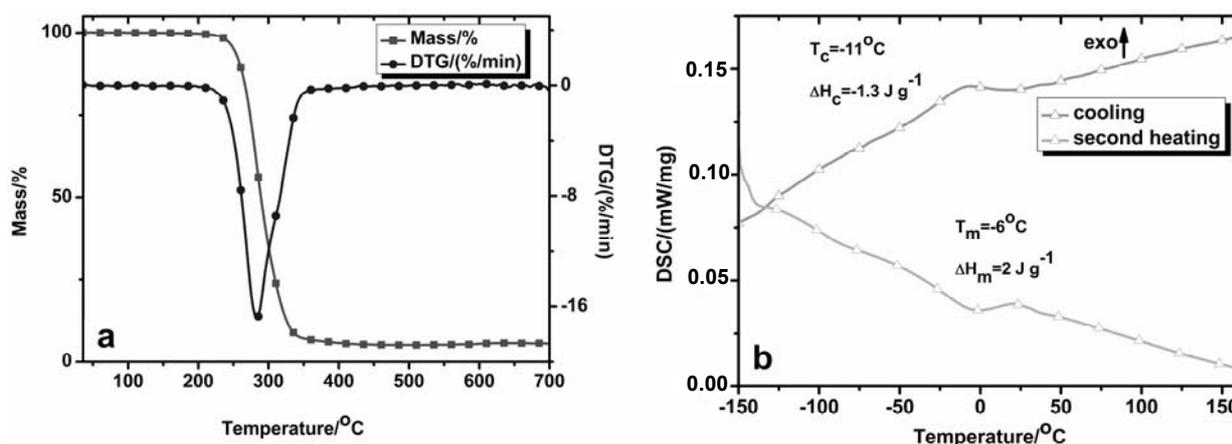

Fig. 5 – TG-DTG (left-a) and DSC (right-b) curves for the compound **1** recorded in nitrogen atmosphere.
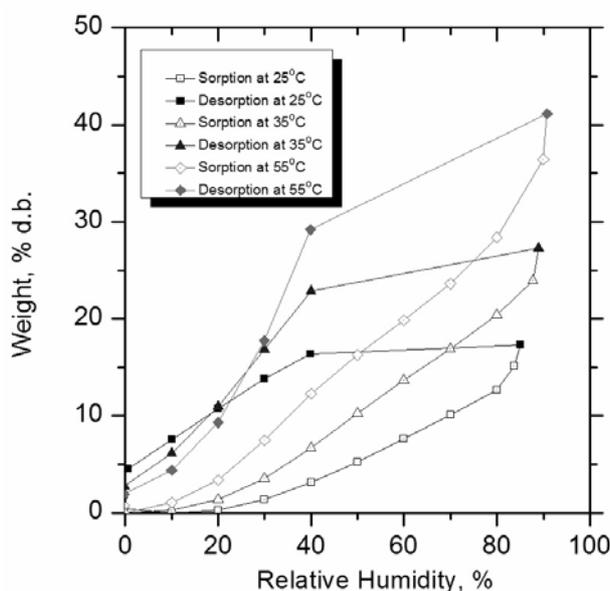

Fig. 6 – Water vapour sorption-desorption isotherms of the isolated compound **1** at different temperatures.

Table 2

Thermal decomposition characteristics

Sample	Step	T (°C)			W_m (%)	W_rez (%)
		T_i	T_{max}	T_f		
1	I	243	283	332	94	5

T_i – initial thermal degradation temperature; T_{max} – temperature that corresponds to the maximum rate of decomposition for each stage evaluated from the peaks of the DTG curves; T_f – final thermal degradation temperature; W_m – mass loss rate corresponding to the T_{max} values; W_{rez} – percentage of residue remained at the end of thermal degradation (700 °C).

EXPERIMENTAL

Materials

3-Aminopropyltriethoxysilane (99%, $d_{20°C}$ = 0.946 g/L) and hydrochloric acid (c=37%) were purchased from Sigma Aldrich and used as such. Methanol p.a. was acquired from Chemical Company.

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 cm⁻¹ range, at room temperature, with a resolution of 2 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 δ values (ppm) relative to the solvent residual peak. The carbon, hydrogen, and nitrogen contents were determined by standard methods. The thermogravimetric analysis was performed on STA 449F1 Jupiter NETZSCH (Germany) equipment. The measurements were made in the temperature range 20-700 °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). A mass of 15 mg of each sample was heated in pierced and sealed aluminum crucibles at a heating rate of 10 °C min⁻¹. Nitrogen atmosphere at a flow rate of 50 mL min⁻¹ was used. The temperature against heat flow was recorded. The device was calibrated using indium according to standard procedures. 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 IGAsorp produced by Hiden Analytical, Warrington (UK).

X-ray Crystallography

Crystallographic measurements for compound **1** were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation. The crystals were placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.[22] The structure was solved by direct methods using Olex2[23] software with the SHELXS[24] structure solution program and refined by full-matrix least-squares on F_0^2 with SHELXL-97.[24] Atomic displacements for non-hydrogen, non-disordered atoms were refined using an anisotropic model. The "use solvent mask" subroutine of Olex2 program[23] was used to account for the scattering from disordered water molecules. Due to this technique, the $R_1(I>2\sigma(I))$ value has been decreased from 0.1295 to 0.0854. The hydrogen atoms have been placed by Fourier Difference accounting for the hybridisation of the supporting atoms and the possible presence of hydrogen bonds in the case of donor atoms. The molecular plots were obtained using the Olex2 program.[23] The main crystallographic data together with refinement details are summarized in Table 3, while the selected bond lengths and angles can be found in Table 4.

CCDC-959469 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

Table 3

Crystallographic data, details of data collection and structure refinement parameters for the compound **1**

	1
Empirical formula	$C_{24}H_{80.36}Cl_8N_8O_{16.18}Si_8$
Formula weight	1248.58
Temperature/K	293
Crystal system	tetragonal
Space group	*P*4/mnc
a/Å	21.0406(8)
b/Å	21.0406(8)
c/Å	32.7349(14)
α/°	90
β/°	90
γ/°	90
V/Å3	14491.9(10)

Table 3 (continued)

Z	8
D_{calc}/mg/mm^3	1.145
μ/mm^{-1}	0.492
Crystal size/mm^3	$0.05 \times 0.05 \times 0.10$
θmin, θ max(°)	4.62 to 59.14
Reflections collected	65905
Independent reflections	7198 [R_{int}=0.1980]
Data/restraints/ parameters	7198/0/280
$R_1{}^a$(I>2σ(I)	0.0854
$wR_2{}^b$(all data)	0.1211
GOF^c	0.954
$\Delta\rho_{max}$ and $\Delta\rho_{min}$/e/Å^3	0.37/-0.34

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $^b wR_2 = \{\Sigma[w\,(F_o{}^2 - F_c{}^2)^2]\,/\Sigma[w(F_o{}^2)^2]\}^{1/2}$;
^{c}GOF $= \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]\,/(n - p)\}^{1/2}$, where n is the number of reflections and p is the
total number of parameters refined.

Table 4

Selected bond lengths (Å)°and angles (°) for **1**

Distances	**1^a(NH$_3$Cl)**
Si1-O1	1.612(6)
Si1-O4	1.607(5)
Si1-O5	1.615(3)
Si2-O1	1.592(6)
Si2-O2	1.617(6)
Si2-O6	1.611(3)
Si3-O2	1.643(6)
Si3-O3	1.609(5)
Si3-O7	1.614(3)
Si4-O3	1.602(5)
Si4-O4	1.624(6)
Si4-O8	1.614(3)

Angles	
O1Si1O4	108.7(5)
O1Si1O5	110.2(5)
O4Si1O5	108.9(5)
O1Si2O2	110.0(5)
O1Si2O6	108.9(5)
O2Si2O6	109.6(6)
O2Si3O3	109.1(4)
O2Si3O7	108.8(5)
O3Si3O7	109.3(4)
O4Si4O3	108.8(4)
O3Si4O8	109.5(4)
O4Si4O8	108.7(4)
Si1O1Si2	147.2(5)
Si2O2Si3	148.2(5)
Si3O3Si4	150.3(5)
Si1O4Si4	152.1(5)
Si4O5Si2	147.2(9)[1]
Si2O6Si2	150.4(8)[1]
Si3O7Si3	147.9(7)[1]
Si4O8Si4	145.7(6)[1]

Symmetry codes used to generate equivalent atoms: [1] x,y,1-z, [2] 1-x,-y,-z, [3] -x,-y,-z, [4] 1-x,1-y,1-z.
^{a} See Fig. 1 for atom numbering

Procedure

8.4 g (0.038 moles) 3-Aminopropyltriethoxysilane, 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. Colourless crystals suitable for XRD were formed after twenty days from solution (raw crystals yield: 1.78, 32 wt%). After X-ray analysis, the sample was dried 24 hours at 100 °C in vacuum. Elemental analysis, wt%: found: C, 24.40; H, 6.09; N, 9.50; calculated for the molecular formulae without lattice water, $C_{24}H_{72}N_8O_{12}Si_8Cl_8$ (M=1173.22 g/mol): C, 24.54; H, 6.13; N, 9.54. IR (KBr pellet, cm^{-1}): 430w, 470m, 542m, 671vw, 699m, 708m, 749w, 791vw, 808w, 824w, 910m, 923m, 935m, 996m, 1052m, 1109vs, 1141vs, 1215m, 1243m, 1309w, 1335w, 1407vw, 1474w, 1502s, 1579w, 2890m, 2914m, 3016m, 3191w, 3436vw. ^{1}H-NMR (400.13 MHz, DMSO-d$_6$): 0.74 (t, J=8.2 Hz, Si-CH_2-), 1.74 (pen, J=8 Hz, Si-CH$_2$-CH_2-), 2.79 (t, J=7.6 Hz, Si-CH$_2$-CH$_2$-CH_2-NH3Cl), 8.26 (s, CH$_2$-CH$_2$-CH$_2$-NH_3Cl); intensities ratio: 1:1:1:1.5 (Fig. 1). ^{13}C-NMR (100.6 MHz, DMSO-d$_6$): 8.40 (Si-CH$_2$-), 20.58 (Si-CH$_2$-CH$_2$-), 40.99 (Si-CH$_2$-CH$_2$-CH_2-NH$_3$Cl). ^{29}Si-NMR (79.49 MHz, DMSO-d$_6$): -66.49 (Fig. 2).

CONCLUSION

The acid hydrolysis product (**1**) of 3-aminopropyltriethoxysilane was isolated and its structure was determined by elemental and spectral analysis and X-ray single crystal diffraction. NH$_2$ group resulted in chloroammonium form. An elongation was observed in inner cage of the structure. The compound **1** shows a complex three-dimensional supramolecular architecture. The compound has a relatively low thermal stability, it decomposes suddenly, in one step when remains a very small amount of residue. The moisture sorption capacity increases with increasing temperature and humidity.

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