



Condensation reaction through base assistance within $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$

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ABSTRACT

When the polycyclic alumosiloxane $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, which may be isolated as the diethyl ether adduct $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 4\text{OEt}_2$, is allowed to react with the double *N*-methylpiperidine (nmp) adduct of monochloroalane, $\text{AlH}_2\text{Cl} \cdot 2\text{nmp}$ (**1**) (crystal structure analysis), the polycycle $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) is obtained. Compared to the starting material and apart from the coordinating bases, the compound formally has lost two water molecules. The structure of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) can be derived from $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ by substituting the central $\text{Al}_4(\text{OH})_4$ motif through an Al_4O_2 entity which consists of a central Al_2O_2 ring coordinated to two further aluminum atoms through almost trigonal planar oxygen atoms. Using tris(ethylene)diamine (ted) as base and reacting it with $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, we have been able to isolate and completely characterize an intermediate on the way to these formally condensed alumosiloxane polycycles like in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**). It has the composition $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**) and has, compared to the starting material, the same number of hydrogen, oxygen, aluminum and silicon atoms within the inner molecular framework. Nevertheless, its structure is very different: whereas half of the molecule is structurally similar to $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, with OH-groups forming hydrogen bridges to the nitrogen atoms of ted and connecting two aluminum atoms, the other half contains a unique oxygen atom which is in an almost planar trigonal bonding mode to three aluminum atoms. Furthermore, this part of the molecule has an aluminum atom to which a water molecule is coordinated, one of the hydrogen atoms being involved in hydrogen bonding to a further tris(ethylene)diamine (ted). This structure gives some important insights in the possible mechanism of the “condensation reaction” within $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$.

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1. Introduction

The polycyclic alumosiloxane $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, which may be obtained by treatment of diphenylsilanediol, $\text{Ph}_2\text{Si}(\text{OH})_2$, with *tert*-butoxyalane, $[\text{H}_2\text{AlO}^t\text{Bu}]_2$ [**1**], is a representative of a molecular alumosilicate with hydrogen atoms in the place of metallic elements [2–4]. Molecular alumosilicates are of general interest because one can mimic reactions of solid alumosilicates, like ion exchange reactions, in an organic solvent. Furthermore, mechanistical questions can be addressed to more easily than in a solid. We have been interested in the hydrolysis of this alumosiloxane and have found that for example the compound $(\text{Ph}_2\text{SiO})_{12}[\text{AlO}(\text{OH})]_6[\text{Al}(\text{OH})_3] \cdot 3\text{OEt}_2$ can be obtained in a crystalline form which contains in the centre of the polycyclic compound an $[\text{Al}(\text{OH})_6]^{3-}$ moiety [5]. On the other side, as the molecule $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ contains several OH-groups which

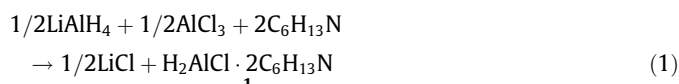
are bonded to the aluminum atoms, also condensation reactions may be envisaged. Indeed, when $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ is allowed to react with hexamethyldisilazane $\text{H}-\text{N}(\text{SiMe}_3)_2$ in the presence of pyridine (py) we could isolate a product which compared to the starting compound lacks two water molecules. The composition of this compound was established to be $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ and it was found by X-ray structure determination that this molecule contained an $\text{Al}_2[\text{O}(\text{Al})]_2$ -ring in the place of the $\text{Al}_4[\text{O}(\text{H})]_4$ eight-membered cycle within $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, the siloxane parts of the two molecules being very similar [6]. Formally, $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ is related to $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ by a condensation reaction within the aluminum hydroxide part of the molecule. To further elucidate this condensation, we have investigated the process in two ways: one was to use other bases in the place of the mixture of hexamethyldisilazane and pyridine with $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ and the other to abstract the protic hydrogen atoms within the inner $\text{Al}_4(\text{OH})_4$ ring by reaction with aluminum hydrides through dihydrogen elimination. The results obtained with tris(ethylene)diamine (ted) and with a double *N*-methylpiperidine (nmp) adduct of chloroalane are summarized in the following.

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2. Results and discussion

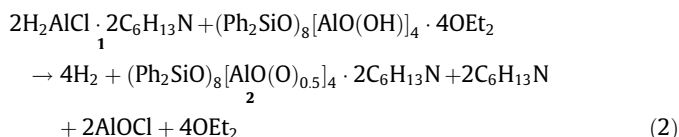
2.1. Synthetic aspects

The monochloroalane stabilized by two *N*-methylpiperidine molecules has been obtained using a route introduced by Wiberg and Schmidt [7,8]. As shown in Eq. (1), lithium aluminum hydride and aluminum chloride are mixed in a 1:1 ratio in diethyl ether and after separation of the lithium chloride salt, the monochloroalane is obtained as nmp-bisadduct through addition of the base and crystallization.



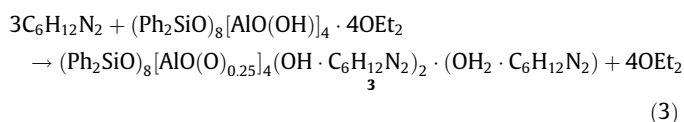
The monochloroalane adduct is characterized by NMR- and IR-spectroscopy as well as by X-ray diffraction (see below). Whereas in the ^1H and ^{13}C NMR spectra the nmp ligand of the adduct can clearly be attributed to the signals, the presence of the Al–H bond is inferred by the observation of the vibrational mode at 1769.71 cm^{-1} in the IR-spectrum.

The reaction of $\text{H}_2\text{AlCl} \cdot 2\text{nmp}$ (**1**) with $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ is performed in a 2:1 ratio in diethyl ether solution (Eq. (2)).



Whereas the evolution of hydrogen may be deduced from the appearance of bubbles in the reaction mixture, the formation of AlOCl only follows from the analytical examination of the solid residue (see Section 3). The new compound $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) is obtained in a crystalline form by extraction from the residue with toluene and recrystallisation as a toluene solvate. The phenyl groups as well as the hydrogen atoms of nmp can be clearly distinguished in the ^1H and ^{13}C NMR spectra. Interestingly, two separate singlets are found for the silicon atoms in the ^{29}Si NMR spectrum. This is in accord with the molecular structure of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**), which has a crystallographic inversion centre and, assuming free rotation of the nmp ligands around the N–Al bonds, deviates only slightly from the $2/m$ (C_{2h}) symmetry (see below). Interestingly, the product contains no chlorine atoms although compounds like $\{[\text{O}-(\text{Ph})_2\text{Si}-\text{O}-\text{Si}(\text{Ph})_2-\text{O}]\text{AlCl} \cdot \text{thf}\}_2$ or $[\text{O}-(\text{Me})_2\text{Si}-\text{O}-\text{Si}(\text{Me})_2-\text{O}]_2(\text{AlCl}_2)_2(\text{AlCl})$ have been reported [9,10].

The new polycycle $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**) (ted = tris(ethylene)diamine) is produced by simple interaction of ted on $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ as shown in Eq. (3).



The product from Eq. (3) is obtained by crystallization from the toluene solution as a solid compound which contains four molecules of toluene per molecule in the crystal lattice. The ^1H NMR and ^{13}C NMR spectra are in accord with a ratio of three ted molecules being connected to the starting alumosiloxane replacing all diethyl ether molecules. The different OH-groups are identified on the basis of the structure determination by X-ray diffraction. Nevertheless, it can be concluded from the IR-spectrum of the product that only one type of OH-group is found as a sharp resonance at 3640 cm^{-1} . Comparing the results of the structure determination (see below) with this finding seems to indicate that all $\text{N} \cdots \text{H} \cdots \text{O}$ hydrogen bridges have to be described as $\text{N}^+ \cdots \text{H} \cdots \text{O}^-$ with

a bond between nitrogen and hydrogen, giving the nitrogen atom an ammonium type character. Unfortunately, the $\text{N}-\text{H}^+$ absorbance is not clearly visible in the spectrum as it seems to be occluded by the C–H frequencies. In other words: only one of the four OH-groups is not engaged in a hydrogen bonding to nitrogen, which is nicely reflected in the single and sharp resonance line in the $3300\text{--}3700\text{ cm}^{-1}$ region of the spectrum.

2.2. Structural aspects

The crystal structure determinations on $\text{H}_2\text{AlCl} \cdot 2\text{nmp}$ (**1**), $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) and $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**) have been performed on single crystals. The crystal of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) contained one disordered toluene molecule per formula unit and in the case of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**) all together eight toluene molecules are located in the unit cell. The structures have been solved using the SHELX-program [11] and the most relevant data are compiled in Table 1. A selection of the most important distances and angles in these molecules can be found in Table 2, whereas access to the full data is given through the Cambridge Crystallographic Data Centre [12].

The new compound $\text{H}_2\text{AlCl} \cdot 2\text{nmp}$ (**1**) is a representative of base stabilized monochloroalanes and a drawing of this molecule is depicted in Fig. 1 [13]. The compound has a twofold symmetry (the twofold axis running through the Al–Cl bond) in the crystal and has a trigonal bipyramidally coordinated aluminum atom with an almost linear N–Al–N entity (deviation from linearity: $2.7(1)^\circ$). Compared to the only other published $\text{H}_2\text{Al}-\text{Cl} \cdot 2\text{base}$ structure, namely chlorobis(quinuclidine) alane [14], the N–Al and Cl–Al distances in $\text{H}_2\text{AlCl} \cdot 2\text{nmp}$ (**1**) are longer by 0.02 Å, respectively 0.01 Å; also the deviation from linearity in chlorobis(quinuclidine) is more prominent by 4.1° .

The condensation product $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) is centrosymmetric as may be seen from Fig. 2. To a central Al_2O_2 ring four O– Ph_2Si –O– SiPh_2 –O units are linked in such a way, that four further eight-membered $\text{Al}_2\text{O}_4\text{Si}_2$ rings are formed. Whereas the aluminum atoms Al(1) and Al(1') are in a tetrahedral oxygen environment, the symmetrically equivalent atoms Al(2) and Al(2') have an nmp base coordinated through its nitrogen atom also obtaining a fourfold coordination sphere. No hydroxyl group is present in the molecule and compared to the original $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ the new molecule has two water molecules less, in a formal sense. As already stated in the introduction, this compound resembles structurally to $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ with the exception that the pyridine molecules serve as donors in the place of *N*-methylpiperidine (nmp) [6]. Both compounds are centrosymmetric and the central $\text{Al}_2[\text{O}(\text{Al})]_2$ ring in both molecules exhibits similar distances and angles. In $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$, the Al–O distances within the ring are shorter (Al–O (mean) = $1.807(5)\text{ \AA}$), but the corresponding bond length to Al(2)–O(1) in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ is longer ($1.775(5)\text{ \AA}$) (see also Table 2). It can be estimated from the proton affinity of *N*-methylpiperidine (which is 971.1 kJ/mol) that this base should attract the hydrogen atoms in a stronger way compared to pyridine (928 kJ/mol) [15]. This somewhat simplistic prediction is not consistent with the observed bonding distance of Al(2)–N(1) of $1.958(2)\text{ \AA}$ in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) compared to the corresponding Al–N distance in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ ($1.934(4)\text{ \AA}$) [6]. Clearly here the bulkiness of the ligands plays an important part, the pyridine having less steric strain to enter the coordination sphere of the aluminum atom. The O(1) atom in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{nmp}$ (**2**) has an angle sum of 358.2° whereas the corresponding atom in $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4 \cdot 2\text{py}$ has a sum of angles of 359.3° . Both oxygen atoms should be considered to be in an almost planar aluminum environment.

Table 1Crystal data of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4(\text{OH}\cdot\text{ted})_2(\text{OH}_2\cdot\text{ted})$ (**3**), $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4\cdot 2\text{nmp}$ (**2**) and $\text{AlH}_2\text{Cl}\cdot 2\text{nmp}$ (**1**).

Empirical formula	$\text{C}_{114}\text{H}_{120}\text{Al}_4\text{N}_6\text{O}_{16}\text{Si}_8 \times 4\text{C}_7\text{H}_8$	$\text{C}_{108}\text{H}_{106}\text{Al}_4\text{N}_2\text{O}_{14}\text{Si}_8 \times \text{C}_7\text{H}_8$	$\text{C}_{12}\text{H}_{28}\text{AlClN}_2$
Formula weight	2531.34	2080.72	262.79
T (K)	153(2)	150(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Pbcn$
<i>Unit cell dimensions</i>			
a (Å)	14.6729(10)	14.3357(3)	12.0452(12)
b (Å)	15.8940(13)	14.7160(4)	12.6545(12)
c (Å)	30.772(2)	15.6775(4)	9.8399(9)
α (°)	81.045(4)	62.6340(10)	
β (°)	79.283(3)	83.0770(10)	
γ (°)	74.773(3)	65.3290(10)	
Volume (Å ³)	6760.3(9)	2658.69(11)	1499.9(2)
Z	2	1	4
Density (calculated) (Mg/m ³)	1.244	1.300	1.164
Absorption coefficient (mm ⁻¹)	0.170	0.199	0.294
F(0 0 0)	2676	1094	576
Crystal size (mm ³)	$0.57 \times 0.31 \times 0.18$	$0.50 \times 0.26 \times 0.15$	$0.48 \times 0.3 \times 0.22$
θ Range for data collection (°)	1.34–28.38	1.47–26.42	3.12–44.66
Index ranges	$-19 < h < 19, -21 < k < 21, -41 < l < 41$	$-17 < h < 17, -18 < k < 14, -19 < l < 18$	$-19 < h < 23, -24 < k < 22, -19 < l < 17$
Reflections collected	123 752	38 569	24 735
Independent reflections	33 723 [$R_{\text{int}} = 0.0324$]	10 800 [$R_{\text{int}} = 0.0385$]	5603 [$R_{\text{int}} = 0.0291$]
Completeness to θ (%)	99.5	98.8	92.0
Absorption correction	Multiscan	Multiscan	Multiscan
Maximum and minimum transmission	0.9693 and 0.9097	0.9712 and 0.9077	0.9382 and 0.8718
Refinement method	Full-matrix-block least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	33 723/0/1622	10 800/0/651	5603/0/130
Goodness-of-fit on F^2	1.011	1.027	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0441, wR_2 = 0.1055$	$R_1 = 0.0544, wR_2 = 0.1454$	$R_1 = 0.0299, wR_2 = 0.0817$
R indices (all data)	$R_1 = 0.0710, wR_2 = 0.1218$	$R_1 = 0.0821, wR_2 = 0.1672$	$R_1 = 0.0498, wR_2 = 0.0941$
Largest difference in peak and hole (e Å ⁻³)	0.632 and -0.609	0.599 and -0.412	0.381 and -0.371

Table 2Selected bond distances [Å] and angles [°] of $\text{AlH}_2\text{Cl}\cdot 2\text{nmp}$, $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4\cdot 2\text{nmp}\cdot \text{C}_7\text{H}_8$ and $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4(\text{OH}\cdot\text{ted})_2(\text{OH}_2\cdot\text{ted})\cdot 4\text{C}_7\text{H}_8$.

Cl–Al	2.2221(3)	N(1')–Al–N(1)	177.27(2)	C(6)–N(1)–Al	108.90(3)
Al–N(1)	2.1618(4)	N(1)–Al–Cl	91.36 (1)	C(5)–N(1)–Al	110.16(3)
Al–H(1)	1.544(9)	N(1)–Al–H(1)	89.8(4)	C(1)–N(1)–Al	106.97(3)
N(1)–C(6)	1.4754(6)	Cl–Al–H(1)	117.4(3)		
N(1)–C(5)	1.4906(6)				
N(1)–C(1)	1.4947(6)				
Al(1)–O(1)	1.812(2)	O(2)–Al(1)–O(5)	113.7(1)	O(4)–Al(2)–O(6)	116.3(1)
Al(1)–O(1')	1.815(2)	O(2)–Al(1)–O(1)	114.46(9)	O(4)–Al(2)–O(1)	112.40(9)
Al(1)–O(2)	1.697(2)	O(5)–Al(1)–O(1)	112.47(9)	O(6)–Al(2)–O(1)	111.73(9)
Al(1)–O(5)	1.708(2)	O(2)–Al(1)–O(1')	114.51(9)	O(4)–Al(2)–N(1)	103.5(1)
Al(2)–O(1)	1.755(2)	O(5)–Al(1)–O(1')	112.29(9)	O(6)–Al(2)–N(1)	106.02(9)
Al(2)–N(1)	1.958(2)	O(1)–Al(1)–O(1')	86.67(8)	O(1)–Al(2)–N(1)	105.73(9)
Al(2)–O(4)	1.699(2)	O(2)–Al(1)–Al(1')	124.74(8)		
Al(2)–O(6)	1.701(2)	O(5)–Al(1)–Al(1')	121.57(8)		
Al(1)–O(1)	1.801(1)	O(4)–H(4)	0.72(3)	O(2)–Al(1)–O(1)	107.31(6)
Al(1)–O(2)	1.757(1)	N(3)–H(2)	0.92(2)	O(3)–Al(2)–O(2)	102.80(6)
Al(2)–O(3)	1.750(1)	O(4)–H(2)	1.69(2)	O(3)–Al(3)–O(1)	106.73(6)
Al(2)–O(2)	1.767(1)	N(1)–H(1)	0.97(2)	O(4)–Al(4)–O(1)	108.64(6)
Al(3)–O(1)	1.802(1)	O(3)–H(1)	1.60(2)		
Al(3)–O(3)	1.747(1)	N(5)–H(3)	1.40(3)		
Al(4)–O(4)	1.767(1)	O(2)–H(3)	1.13(3)		
Al(4)–O(1)	1.780(1)				

The third compound $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4(\text{OH}\cdot\text{ted})_2(\text{OH}_2\cdot\text{ted})$ (**3**) is the most interesting one: it can be described as a sort of 1:1 mixture (in a structural sense) between $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ and $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2$ bases. Half of the molecule (Al(1), O(2), Al(2), O(3), Al(3)), indeed, is structurally similar to $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ with OH-entities serving as connecting units between aluminum atoms through oxygen–aluminum interactions (see Fig. 3). As in the pyridine adduct of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4\cdot 4\text{py}$, the OH-groups are involved in hydrogen bridges to nitrogen [16]. The other part of the molecule (Al(1), O(1), Al(4), Al(3)) is quite similar to the

structure of $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2\text{nmp}$ (**2**) with an almost trigonal planar oxygen atom O(1) (sum of angles around O(1) = 357.5°) and a water molecule coordinated to the aluminum atom Al(4). In a formal sense, this water molecule is replacing the nmp ligand in $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2\text{nmp}$ (**2**). The O(1)–Al(1,3,4) distances are very comparable (mean distance 1.794(1) Å). The water molecule which consists of H(2), O(4) and H(4) forms a strong hydrogen bond through H(2) (N(3)–O(4) = 2.60 Å) to one nitrogen atom of ted; so, the H(2) atom seems to be shifted to N(3), forming a type of binding which may be written in the form $\text{N}^+\text{H}\cdots(\text{O}\text{H})^-$.

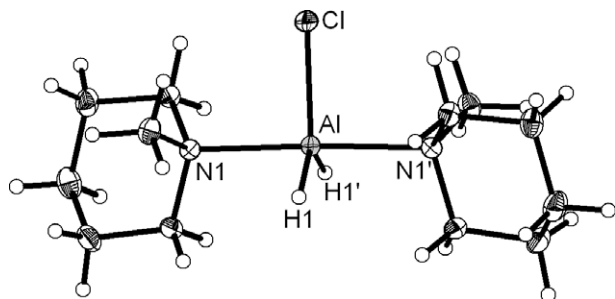


Fig. 1. The molecular structure of $\text{H}_2\text{AlCl}\cdot 2\text{nmp}$ (**1**) with displacement ellipsoids drawn at the 50% probability level [13].

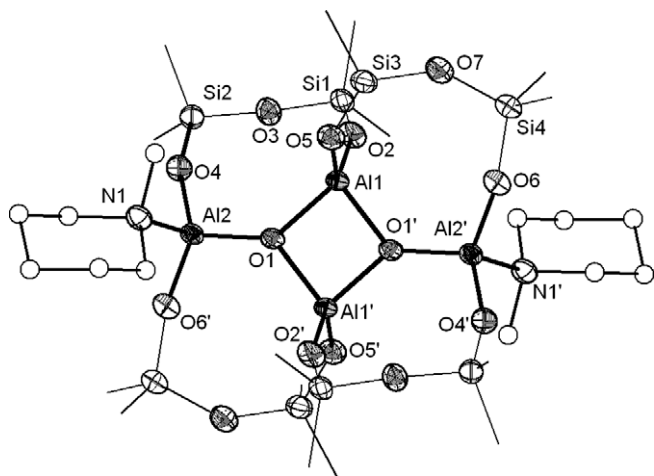


Fig. 2. A structural representation of the inner core of $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2\text{nmp}$ (**2**) with displacement ellipsoids (except carbon atoms) drawn at the 50% probability level. All phenyl groups as well as the hydrogen atoms on the carbon atoms have been omitted for clarity [13].

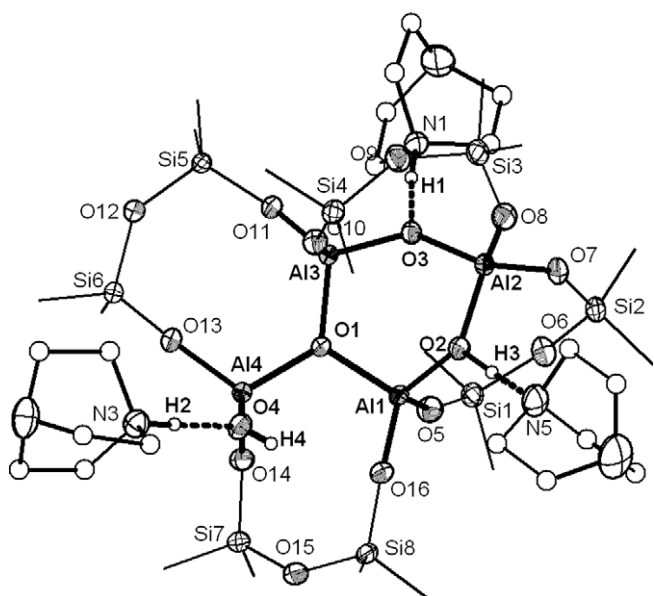


Fig. 3. The inner core of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4\cdot (\text{OH}\cdot\text{ted})_2\cdot (\text{OH}_2\cdot\text{ted})$ (**3**) with displacement ellipsoids (except carbon and hydrogen atoms) drawn at the 50% probability level. All phenyl groups and hydrogen atoms of the ethylene groups have been omitted for clarity [13].

Excluding the ted ligands, $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4\cdot (\text{OH}\cdot\text{ted})_2\cdot (\text{OH}_2\cdot\text{ted})$ (**3**) has as many hydrogen atoms bonded to oxygen as $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$. The two compounds may thus be classified as structural isomers. Moreover, they may be taken as models for transient species in a possible condensation mechanism.

To make this more clear, the molecules $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$, $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4\cdot (\text{OH})_2\cdot \text{OH}_2$ and $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4$ are drawn in a two-dimensional representation in Fig. 4 omitting the coordinated bases. Using these structures, a mechanism may be proposed which starts with a ted base attack on each of the four OH-groups present in the starting material. After proton abstraction, one of the oxygen atoms becomes very basic attacking one of the two adjacent aluminum corners introducing a new Al–O bond from an OH-group. The so formed OH-group being liberated may be attacked by a proton or by an ammonium type $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}^+\text{-H}$ species forming a water entity. The water molecule finally may be displaced by an attack of a further base on the aluminum coordinated to the water entity. Repeating this procedure for a second time will generate a molecule which has two water molecules less and which resembles the condensed product as found for $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2\text{nmp}$ (**2**) or $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4\cdot 2\text{py}$.

3. Experimental

All syntheses were carried out under N_2 atmosphere in a modified “Stock vacuum apparatus”. The solvents (diethyl ether, toluene, tetrahydrofuran) were distilled from sodium and kept under N_2 . C-, H-, N-analyses were measured on a CHN-900 Elemental Analyzer from Fa. Leco Corporation (St. Joseph, Mi, USA). Al and Cl contents follow from complexometric and titrimetric techniques [17,18]. ^1H , ^{13}C , ^{27}Al and ^{29}Si NMR spectra were recorded on a Bruker NMR-spectrometer AC200 in C_6D_6 (internal standard TMS, $\delta = 0.00$). IR-spectra have been measured with Varian 2000 FT-IR-spectrometer.

3.1. Synthesis of $\text{H}_2\text{AlCl}\cdot 2\text{nmp}$ (**1**)

To a suspension of 0.86 g (22.6 mmol) lithium aluminum hydride in 75 mL diethyl ether was dropped a solution of 3.02 g (22.6 mmol) aluminumtrichloride in 75 mL diethyl ether. After 1 h stirring, an excess of 13.77 mL (113 mmol) *N*-methylpiperidine was added drop by drop to the mixture under cooling (ice bath) and stirred for additional 1 h. Around 200 mL hexane were added to the resulting mixture to complete the precipitation of lithium chloride. The chloride salt was separated by filtration and the volume of the solvent mixture reduced at lower pressure to allow the formation 9.15 g (77%) of colorless crystals of $\text{H}_2\text{AlCl}\cdot 2\text{nmp}$.

Anal. Calc. for $\text{C}_{12}\text{H}_{28}\text{AlClN}_2$ (262.79 g/mol): C, 54.84; H, 10.74; N, 10.66; Al, 10.27; Cl, 13.49. Found: C, 53.75; H, 10.79; N, 10.66; Al, 10.30; Cl, 13.18%. NMR (C_6D_6 , TMS): ^1H NMR (200 MHz): $\delta = 2.57\text{--}2.51$ (m, $\alpha\text{-CH}_2\text{-}$, nmp), 2.18 (s, $\text{CH}_3\text{-}$, nmp), 1.33–1.22 (m, $\beta\text{-CH}_2\text{-}$, nmp), 1.16–1.08 (m, $\gamma\text{-CH}_2\text{-}$, nmp); ^{13}C NMR (50.3 MHz): $\delta = 54.38$ (s, $\alpha\text{-CH}_2\text{-}$, nmp), 43.04 (s, $\text{CH}_3\text{-}$, nmp), 24.04 (s, $\beta\text{-CH}_2\text{-}$, nmp), 22.80 (s, $\gamma\text{-CH}_2\text{-}$, nmp); ^{27}Al NMR: $\delta = 119.02$. IR (Al–H) = 1769.7 cm^{-1} .

3.2. Synthesis of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.5}]_4\cdot 2\text{nmp}$ (**2**)

To a suspension of 2 g (0.94 mmol) of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4\cdot 4\text{OEt}_2$ in 50 mL diethyl ether was added drop by drop 0.495 g (1.88 mmol) of $\text{H}_2\text{AlCl}\cdot 2\text{nmp}$ in 30 mL diethyl ether. After 1 day stirring, the ether was evaporated under reduced pressure and 1.45 g (74%) of an insoluble precipitate was obtained. A small amount of this precipitate was overlaid with toluene and crystals

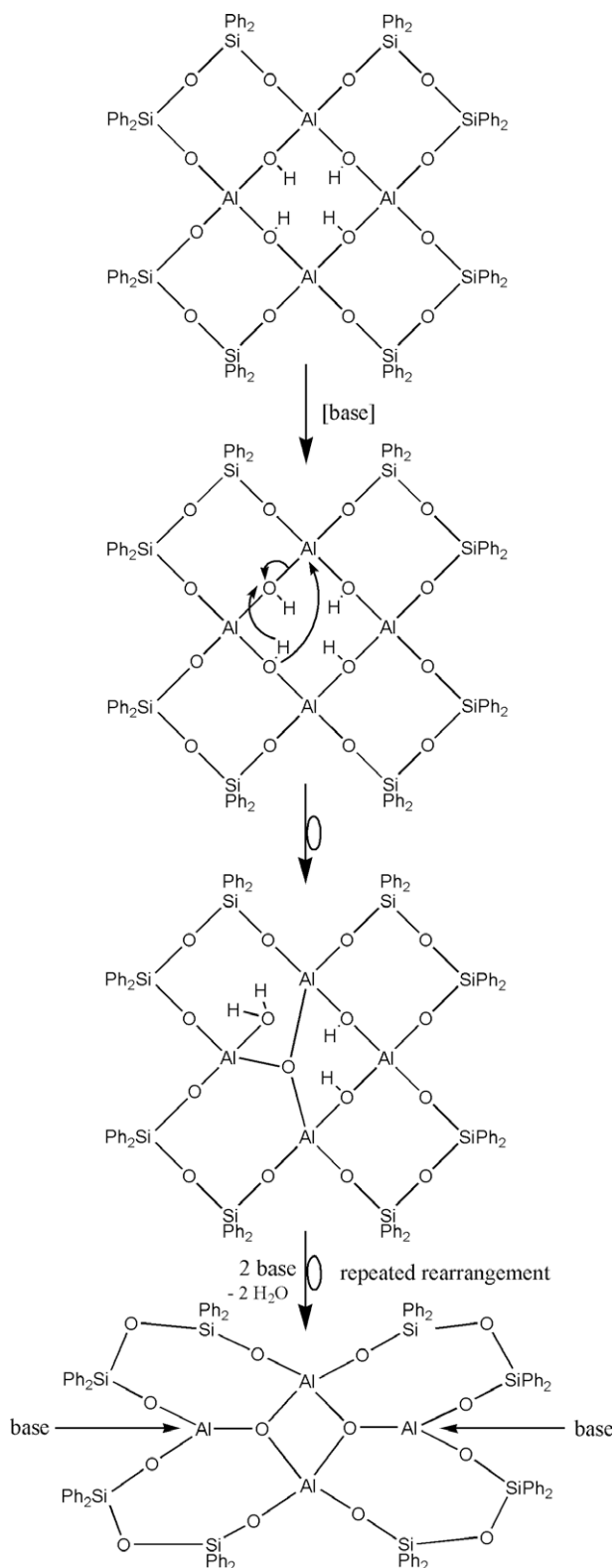


Fig. 4. Possible condensation mechanism within the molecule $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ drawn in a two-dimensional representation.

of $(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4 \cdot 2\text{nmp}$ were obtained from the toluene solution (the first crystal appears only after several weeks).

$\text{C}_{108}\text{H}_{106}\text{Al}_4\text{N}_2\text{O}_{14}\text{Si}_8 \cdot \text{C}_7\text{H}_8$ (2080.72 g/mol). Elemental Anal. Calc. on the basis of an 1:2 solid mixture of $(\text{Ph}_2\text{SiO})_8(\text{AlO}_{1.5})_4 \cdot 2\text{nmp} \cdot \text{C}_7\text{H}_8$ and $\text{AlClO} \cdot \text{nmp}$, $\text{C}_{127}\text{H}_{140}\text{Al}_6\text{Cl}_2\text{N}_4\text{O}_{16}\text{Si}_8$ (2436.01 g/mol): C, 62.62; H, 5.79; N, 2.30; Al, 6.65; Cl, 2.91. Found:

C, 59.68; H, 6.01; N, 1.46; Al, 8.58; Cl, 2.64%. NMR (toluene, C_6D_6 , TMS): ^1H NMR (200 MHz): $\delta = 7.23\text{--}6.83$ (m, Ph), 2.41 (m, $\alpha\text{-CH}_2\text{-}$, nmp), under toluene signal (s, $\text{-CH}_3\text{-}$, nmp), 1.38–1.28 (m, $\beta\text{-CH}_2\text{-}$, nmp), 1.04–0.88 (m, $\gamma\text{-CH}_2\text{-}$, nmp); ^{13}C NMR (50.3 MHz): $\delta = 135.36, 135.07, 131.05, 130.98$ (s, Ph), 32.01 (s, $\alpha\text{-CH}_2\text{-}$, nmp), 29.42 (s, $\text{-CH}_3\text{-}$, nmp), 23.08 (s, $\beta\text{-CH}_2\text{-}$, nmp), 22.75 (s, $\gamma\text{-CH}_2\text{-}$, nmp); ^{29}Si NMR: $\delta = -45.47; -47.35$.

3.3. Synthesis of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**)

About 0.220 g (1.96 mmol) tris(ethylene)diamine (1,4-diazabicyclo[2.2.2]octane) in 25 mL toluene was added dropwise to 1.033 g (0.49 mmol) $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 4\text{OEt}_2$ in 25 mL toluene and stirred at room temperature for 4 h. The solvent was removed under reduced pressure until colorless crystals of 0.892 g (72%) $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted}) \cdot 4\text{C}_7\text{H}_8$ precipitated.

Anal. Calc. for $\text{C}_{114}\text{H}_{120}\text{Al}_4\text{N}_6\text{O}_{16}\text{Si}_8 \cdot 4\text{C}_7\text{H}_8$ (2531.34 g/mol): C, 67.38; H, 6.05; Al, 4.26; N, 3.32. Found: C, 63.83; H, 5.84; Al, 5.10; N, 3.58%. NMR (thf, C_6D_6 , TMS): ^1H NMR (200 MHz): $\delta = 7.64\text{--}7.46$ (m, Ph), 7.20–6.83 (m, Ph), 2.90 (s, ted); ^{13}C NMR (50.3 MHz): $\delta = 140.3, 140.2, 135.27, 135.05, 129.07, 128.89, 127.60, 127.38$ (s, Ph), 45.48 (s, ted); ^{29}Si NMR: $\delta = -47.38$ (s). IR: (characteristic wave numbers) 3640 (OH), 2947 (br, CH), 2876 (br, CH) cm^{-1} .

4. Conclusion

The proposed condensation mechanism discussed above, which is derived by inspection of the crystal structure of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{O})_{0.25}]_4 \cdot (\text{OH} \cdot \text{ted})_2 \cdot (\text{OH}_2 \cdot \text{ted})$ (**3**) in detail, shows nicely that for this condensation reaction quite strong bases like triethylamine (NEt_3) or tris(ethylene)diamine (ted) are needed. Furthermore, the steric requirement must fit: This can easily be shown comparing Et_3N with ted (proton affinities for Et_3N : 981.8 kJ/mol, ted: 963.4 kJ/mol) [15]. Whereas the product of interaction of NEt_3 with $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ is $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 2\text{NEt}_3$ with one side of the polycycle being “closed” by the diphenyl silyl groups in such a way that no further NEt_3 base can interact with the non-coordinated hydroxy groups [4], this is not the case for $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$. Here, the attack of a further, third base is still possible leading to the observed reaction compiled in Eq. (3) and the structure displayed in Fig. 3. Weaker bases like pyridine (proton affinity: 928 kJ/mol) seem to have less effect on the condensation within $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ and instead, the adduct $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4 \cdot 4\text{py}$ is isolated without any noticeable side reaction (compare [16]); in the reaction with a mixture of pyridine and hexamethyldisilazane nevertheless in a minor fraction a condensation reaction is observed leading to the product $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4 \cdot 2\text{py}$ [3]. The reaction of $(\text{Ph}_2\text{SiO})_8[\text{AlO}(\text{OH})]_4$ with $\text{H}_2\text{AlCl} \cdot \text{nmp}$ (**1**) leads directly to the condensation product $(\text{Ph}_2\text{SiO})_8[\text{AlO}_{1.5}]_4 \cdot 2\text{nmp}$ (**2**): here, the evolution of hydrogen and the disappearance of the chloro function indicate another pathway to the formally condensed product.

5. Supplementary material

CCDC 751361, 751362 and 751363 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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