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ARTICLE

Acid-Base Interactions of Pyrazine, Ethyl Acetate, Di-alcohols, and Lysine with the cyclic Alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$ in View of Mimicking $Al_2O_3(H_2O)$ Surface Reactions

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Abstract. The etherate of $(Ph_2SiO)_8[Al(O)OH]_4$ can be transformed into the pyrazine adduct $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3N(C_2H_2)_2N$ (**1**), the ethyl acetate adduct $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3H_3C\text{-}C(O)OC_2H_5$ (**2**), the 1,6-hexane diol adduct $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}2HO\text{–}CH_2(CH_2)_4CH_2\text{–}OH$ (**3**) and the 1,4-cyclohexane diol adduct $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}4HO\text{–}CH(CH_2CH_2)_2CH\text{–}OH$ (**4**). In all compounds the OH groups of the starting material bind to the bases through O–H···N (**1**) or O–H···O hydrogen bonds (**2**, **3**, **4**) as found from single-crystal X-ray diffraction analyses. Whereas in **1** only three of the central OH groups bind to the pyrazines, in **2** two of them bind to the same carbonyl oxygen atom of the ethyl acetate resulting in an unprecedented O–H···O···H–O double hydrogen bridge. The hexane diol adduct **3** in the crystal forms a one-dimensional coordination polymer with an intramolecularly to two OH groups grafted hexane diol loop, while the second hexane diol is connecting intermolecularly. In the cyclohexane diol adduct **4** all OH groups of the central $Al_4(OH)_4$ ring bind to different diols, leaving one alcohol group per diol uncoordinated. These "free" OH groups form an $(O\text{-}H\cdots)_4$ assembly creating a three-dimensional overall structure. When reacting with $(Ph_2SiO)_8[Al(O)OH]_4$ lysine loses water, turns into the cyclic 3-amino-2-azepanone, and transforms through chelation of one of the aluminum atoms the starting material into a new polycycle. The isolated compound has the composition $(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2{\cdot}4\ C_6H_{12}N_2O{\cdot}6(CH_2)_4O$ (**5**).

Introduction

Surfaces and coatings of Al_2O_3 have a high application potential in live sciences and medicine due to their hardness, low conductivity, protective properties against corrosion and their special cellular behavior.[1,2] Especially the behavior of nano structured Al_2O_3 vs. fibroblasts and osteoblasts has attracted our attention in the past years.[3] When used in a living organism Al_2O_3 surfaces are mostly in contact with water which has impact on the surface chemistry: even on crystalline surfaces of the most stable phase α-Al_2O_3 equilibria with water have been detected, showing the generation of OH groups.[4,5] Concerning interactions with peptides a deeper insight into the chemical processes, which occur on the surface of Al_2O_3/H_2O could be extremely helpful. In order to have a profounder perception in the behavior of Al-O(H)-Al moieties towards functional groups we have included and stabilized this atomic arrangement in a molecule and have reacted it with amines, alcohols, ethers, carbonyl compounds etc. in order to get distinct and isolable compounds in view of the possible structures on Al_2O_3/H_2O surfaces. The overall goal is to get indirect information in the molecular processes on surfaces and thus to mimic their reactivity.

Since several years we have studied molecular compounds, which have formally an OAl(OH) entity within their framework.[6] The title compound $(Ph_2SiO)_8[Al(O)OH]_4$, which is a combination of an oligomeric siloxane and OAl(OH), can be easily obtained as an adduct with three diethyl ether molecules[7] (one further diethyl ether is included in the van der Waals lattice) and has served as target for studying several cases of base interactions. The compound contains an $Al_4[O(H)]_4$ eight-membered cycle with four –O–Ph_2Si–O–SiPh$_2$–O– handles, always connecting two aluminum atoms. In Figure 1 the compound (symmetry S_4) is sketched indicating that the four hydrogen atoms of the inner ring are pointing in two obverse directions. We have been able to show, that these acidic hydrogen atoms can bind to Lewis-bases which have either a nitrogen or oxygen atom as basic center. Depending on the size, structure and functionality of the base this can lead to different structure types (see Figure 1).[6]

In this article we report on some new structures which have not been described before and which exemplify the extraordinary chemical and structural versatility of base adducts of $(Ph_2SiO)_8[Al(O)OH]_4$. By use of ethyl acetate, we have found

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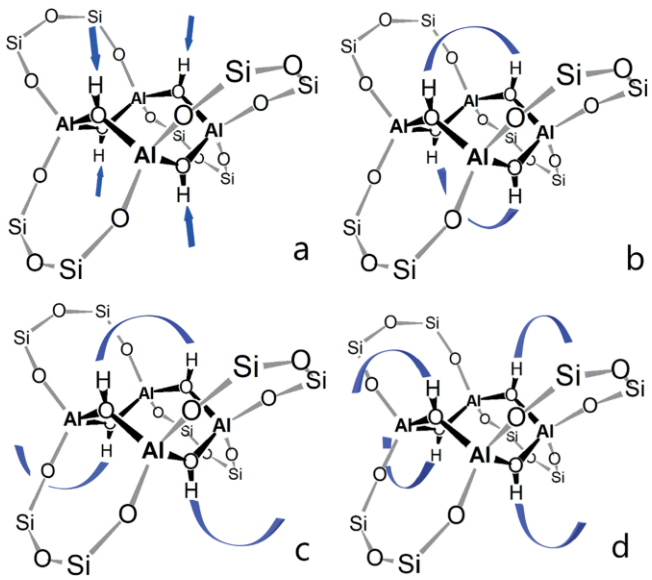

Figure 1. A three-dimensional representation (a) of the alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$, omitting the phenyl groups on the silicon atoms, indicating the pathways (arrows) of Lewis-base interactions with the O-H groups. Depending on the steric demand of the bases two, three or four bases can simultaneously coordinate to the molecule.[6] Using bifunctional bases (drawn as arcs) like diamines of the type $H_2N–(CH_2)_n–NH_2$ or 4,4'-bipyridine and azo-bipyridines may generate intra- (b) and intermolecular assemblies (c, d).[6,8] The intermolecular assemblies may lead to one-, two- or three-dimensional polymers.[6,8]

for the first time an organic base which interacts with two of the OH groups simultaneously through one oxygen atom forming a bridge. Pyrazine, in contrast to pyridine,[9] can only coordinate to three of the four OH groups. The two di-alcohols 1,6-hexanediol and 1,4-cyclohexanediol when reacted with $(Ph_2SiO)_8[Al(O)OH]_4$ differ considerably in their crystal structures. Finally, we have succeeded for the first time to isolate a compound when reacting $(Ph_2SiO)_8[Al(O)OH]_4$ with an amino acid like lysine. The alumosiloxane polycycle in this reaction is chemically and structurally transformed. This gives a first idea about atomic interactions of amino acids with Al_2O_3, respectively OAlOH entities and may be of more general meaning for Al_2O_3 surface reactions of amino-acids and peptides, which are currently under study.[10,11]

Results and Discussion

Syntheses

The alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3OEt_2$[7] has been reacted with pyrazine, ethyl acetate, 1,6-hexane diol and 1,4-cyclohexane diol in order to get an exchange of the bases on the alumosiloxane. The reactions were performed in organic solvents (see Experimental Section) with at least a fourfold molar excess of the bases (Scheme 1).

The products **1–4** of these reactions are obtained by crystallization in high yields and are characterized by IR and NMR spectroscopy. They crystallize frequently with solvent molecules in the crystal, which are acting as space-fillers in the van der Waals lattice: **1** with 1 toluene, **3** with 1 benzene and 1 toluene and **4** with 3 toluene molecules (see Experimental Section). As can be seen from the formulae only in the case of the 1,4-cyclohexane diol 4 bases are coordinated while in the other cases there are 3 (**1**, **2**) or only 2 (**3**). The number of bases binding to $(Ph_2SiO)_8[Al(O)OH]_4$ in the crystalline product is independent of the stoichiometry chosen between the reaction partners. So even a 1:6 ratio between $(Ph_2SiO)_8[Al(O)OH]_4$ and pyrazine leads to the same product. The most important information in the IR spectra can be obtained from the O-H absorption region, as the characteristic OH bands of $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3OEt_2$ at 3617 and 3540 (Sh) cm^{-1} are shifted to other values due to base coordination to the Al-OH groups (see Experimental Section). In the case of compound **2** two carbonyl frequencies at 1697 and 1666 cm^{-1} are found in accordance with the two different binding modes of the ethyl acetate molecules found in the crystal structure. In the ^1H NMR spectra of the dissolved products the integral ratio of the aliphatic to the phenyl groups may serve as a first, crude hint to the number of base molecules coordinated to the alumosiloxane, while in the ^{13}C and ^{29}Si NMR spectra the chemical displacements indicate new products without structural information. The only way to confirm the structures has been in all cases by X-ray diffraction on single crystals.

$(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3OEt_2 + 4L$ →
- $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3L$ — **1**: $L = N(C_2H_2)_2N$; **2**: $L = MeC(O)OEt$
- $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}2L$ — **3**: $L = HOCH_2(CH_2)_4CH_2OH$
- $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}4L$ — **4**: $L = HOCH(CH_2CH_2)_2CHOH$

Scheme 1.

While the reactions discussed so far perform without structural alteration of the alumo-siloxy polycycle this becomes different when lysine is used as reactant (Scheme 2).

$2(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3OEt_2 + 4R/S\text{-}H_2N\text{-}(CH_2)_4\text{-}C(H)(NH_2)\text{-}COOH + 6THF - 5H_2O - 6OEt_2 \rightarrow$

$(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2{\cdot}4R/S\text{-}H_2N\text{-}C(H)\text{-}(CH_2)_4\text{-}C(O)\text{-}N\text{-}H{\cdot}6(CH_2)_4O$ (**5**)

Scheme 2.

The formula for **5** is based on the X-ray structure determination (vide infra) although from the NMR spectroscopic data (^{29}Si, ^1H NMR) it can be concluded, that the original alumosiloxy polycycle has been altered. Lysine, which was used as a mixture of the enantiomers, during the reaction is transformed to its cyclic anhydride 3-amino-2-azepanone. This is not surprising, as Al_2O_3 surfaces are known to catalyze this reaction.[12] It can not be excluded that on dissolution of lysine in boiling toluene (see Experimental Section) also traces of 3-amino-2-azepanone form, although this condensation reaction is reported to proceed very slowly.[12]

Structures

The result of the structure analysis on $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3N(C_2H_2)_2N$ (**1**) is depicted in Figure 2. As already stated,

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there are only three pyrazine molecules coordinated to one alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$ whereas there are four when pyridine is interacting with $(Ph_2SiO)_8[Al(O)OH]_4$.[9] Although both aromatic bases are similar in shape the pyridine is polar and more basic than pyrazine: the proton affinity of pyridine in the gas phase is 930 kJ/Mol whereas for pyrazine it is 877 kJ·mol^{-1}.[13] In the crystal a further toluene molecule per formula is incorporated in the van der Waals lattice.

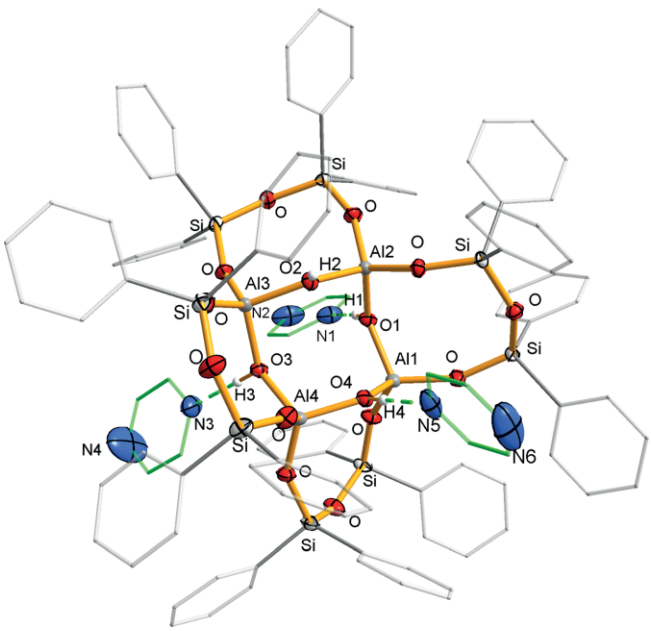

Figure 2. Molecular structure of $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3N(C_2H_2)_2N$ (**1**) with thermal ellipsoids (50 %) at Si, Al, O, N, and stick models for other atoms (the toluene molecule in the crystal lattice is omitted for clarity). The bonds within the pyrazine molecules are in green. Some pertinent bond lengths /Å and angles /°: Al(1)–O(5) 1.699(1), Al(1)–O(16) 1.701(1), Al(1)–O(4) 1.783(1), Al(1)–O(1) 1.792(1), Al(2)–O(8) 1.689(1), Al(2)–O(7) 1.701(1), Al(2)–O(1) 1.773(1), Al(2)–O(2) 1.819(1), Al(3)–O(10) 1.699(1), Al(3)–O(11) 1.703(1), Al(3)–O(3) 1.783(1), Al(3)–O(2) 1.809(1), Al(4)–O(14) 1.701(1), Al(4)–O(13) 1.707(1), Al(4)–O(4) 1.781(1), Al(4)–O(3) 1.805(1), mean values: Si–O(Al) 1.606(3) Si–O(Si) 1.630(4); Al(2)–O(1)–Al(1) 125.60(7), Al(3)–O(2)–Al(2) 131.92(7), Al(3)–O(3)–Al(4) 127.00(7), Al(4)–O(4)–Al(1) 128.44(7). Hydrogen bonds: O(1)···N(1) 2.614(4), O(3)···N(3) 2.666(4), O(4)···N(5) 2.610(4); O(1)–H(1)···N(1) 171.3(8), O(3)–H(3)···N(3) 174.4(8), O(4)–H(4)···N(5) 178.9(8).

This higher basicity of pyridine compared to pyrazine is reflected in stronger O–H···N hydrogen bridges in $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}4N(CH)_5$[8] [N···O = 2.55(1) Å, adjacent Al–O bonds to O–H = 1.769(3) Å] compared to **1** [N···O = 2.63(1) Å, adjacent Al–O bonds to O–H = 1.787(9) Å] (Figure 2). As explained in a former review article, the Al–O bond lengths adjacent to the O-H groups in the ring are a very good indicator for hydrogen bonds in alumo-siloxanes as they reflect the partial charge at the oxygen atom, when the hydrogen atom of the O-H group is engaged in bonding: the more they are short the more the hydrogen atom of the OH group is removed by the base.[6] In the molecule **1** this difference can be nicely seen when comparing O(1), O(3) and O(4) with the O(2) atom [mean O(2)-Al = 1.814(5) Å], which has no base interaction (see caption of Figure 2).

The molecule **1** has no higher symmetry as the central Al_4O_4 ring molecule is not symmetrically coordinated by the pyrazine molecules. The void at the O(2)–H(2) direction within the molecule is filled up by phenyl groups on silicon, which are accommodated in this place. The Si–O and Al–O(Si) distances (Figure 2) are not affected by distortion and compare well with other alumosiloxanes.[6] Although pyrazine is a double base, it is to small to execute intermolecular bonding between different alumosiloxanes.

In Figure 3 the molecular structure of the acid-base adduct between $(Ph_2SiO)_8[Al(O)OH]_4$ and ethyl acetate, $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3H_3C–C(O)OC_2H_5$ (**2**), is shown. The compound has no higher point symmetry, but by neglecting the ethyl acetates a deviation from the higher symmetry C_2 (2), the pseudo twofold axis passing through O(17), is only minor. In this molecule all OH groups of the central Al_4O_4 cycle are engaged in hydrogen bridges to the carbonyl group of the ethyl acetates. For the first time within the base adducts of $(Ph_2SiO)_8[Al(O)OH]_4$ we have found a single base atom [O(17)] coordinated by **two** OH groups [O(2) and O(4)] simultaneously.[6] Indeed, while O(1)–H(1) and O(3)–H(3) are aligned with different carbonyl groups O(19) and O(21) (O–H···O 140° respectively 155°, see Figure 3) O(2)–H(2) and O(4)–H(4) point to the same oxygen atom O(17). Surprisingly, the O···O distances between O(1) and O(19) resp. O(3) and O(21) are only slightly shorter than those between O(17) and O(2)/O(4) [mean difference: 0.032(9) Å, see also caption of Figure 3] although the hydroxy groups of O(1) and O(3) are solely bonded toone molecule ethyl acetate whereas those of O(2) and O(4) have to share a common base. The H(2)···O(17)···H(4) angle with 99° is quite acute and seems to be compensated by the O–H···O angles of about 135° (compare Figure 3).

A closer look on the Al–O distances in the ring reveals that the bonds with O(1) and O(3) are slightly shorter (mean 1.792 Å) than those with O(2) and O(4) (mean 1.800 Å) as expected from the different types of hydrogen bridging. The O···O distances (see caption of Figure 3) reflect these findings, as they are shorter when O(1) and O(3) are engaged (see above). The mean Al-O value within the ring is 1.796(4) Å (1.792(4) Å when only the mono dentate ethyl acetate is concerned), which – as reference for the O–H···base interaction (see above and[6]) – is longer as in the pyrazine derivative **1** (1.787 Å) in accordance with the lower proton affinity of 836 kJ·mol^{-1} compared to pyrazine (877 kJ·mol^{-1}).[13] The mean Al–O value (in the ring) in **2** is comparable for the one found in the acetone adduct $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}4(H_3C)_2C{=}O$, which has a value of 1.794(4) Å and a proton affinity of 812 kJ·mol^{-1}.[14,13]

The other bond lengths and angles compare well with other base adducts of $Ph_2SiO)_8[Al(O)OH]_4$: so the mean Al–O(Si) bond length in **2** is 1.696(5) Å and consequently shorter than the Al–O bond lengths in the eight membered ring (compare Figure 3).[6] The NMR spectra taken in benzene are not compatible with a pseudo C_2 symmetry (for example the ^{29}Si NMR has only one signal) which means that the structure in the crystal is not representative for the molecule in solution.

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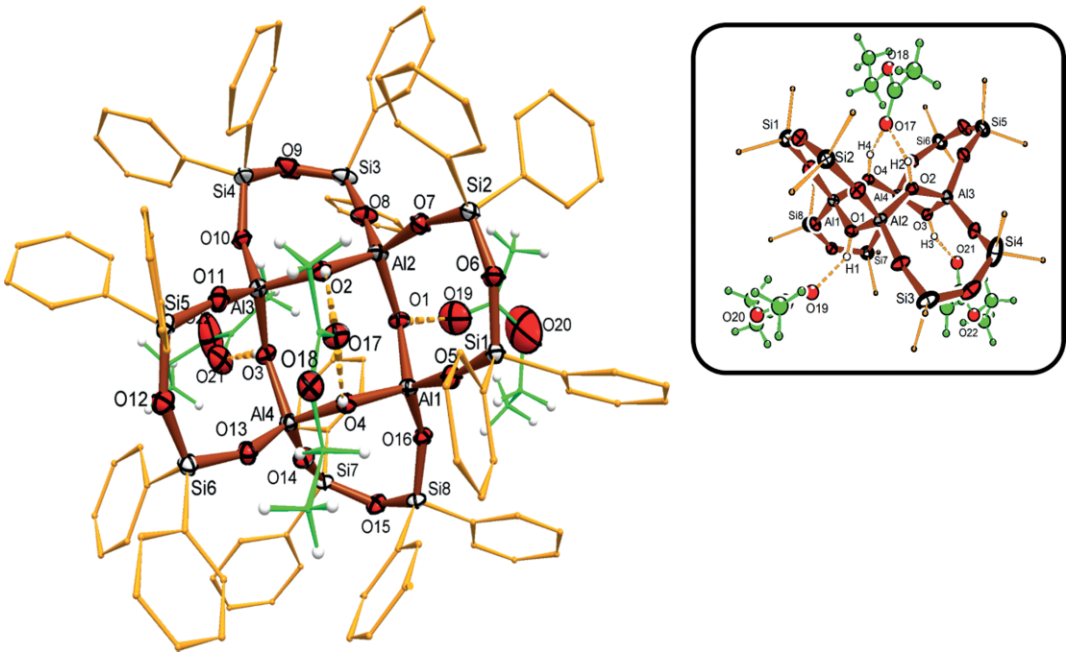

Figure 3. Molecular structure of $(Ph_2SiO)_8[Al(O)OH]_4 \cdot 3\ H_3C\text{-}C(O)OC_2H_5$ (**2**) (left looking on top of the ring, right [insert] from the side) with thermal ellipsoids (50 %) at Si, Al, O and ball and stick models for other atoms. The bonds and the carbon atoms within the ethyl acetyl molecules are in green. Some pertinent bond lengths /Å and angles /°: Al(1)–O(5) 1.694(2), Al(1)–O(16) 1.695(2), Al(1)–O(1) 1.797(2), Al(1)–O(4) 1.799(2), Al(2)–O(8) 1.687(2), Al(2)–O(7) 1.694(2), Al(2)–O(1) 1.792(2), Al(2)–O(2) 1.798(2), Al(3)–O(10) 1.695(2), Al(3)–O(11) 1.710(2), Al(3)–O(3) 1.791(2), Al(3)–O(2) 1.796(2), Al(4)–O(14) 1.684(2), Al(4)–O(13) 1.706(2), Al(4)–O(3) 1.789(2), Al(4)–O(4) 1.805(2), mean bond lengths: Si–O(Al) 1.601(4) Si–O(Si) 1.627(5), carbonyl: C–O(17) 1.233(3), C–O(19) 1.219(6), C–O 1.217(4); Al(2)–O(1)–Al(1) 128.0(1), Al(3)–O(2)–Al(2) 134.1(1), Al(4)–O(3)–Al(3) 128.0(1), Al(1)–O(4)–Al(4) 132.4(1). Hydrogen bonding: O(1)···O(19) 2.640(6), O(2)···O(17) 2.650(7), O(4)···O(17) 2.675(7), O(3)···O(21) 2.619(6); O(19)···H(1)–O(1) 140.3(4), O(21)···H(3)–O(3) 155.0(4), O(17)···H(2)–O(2) 134.9(5), O(17)···H(4)–O(4) 136.4(5), H(4)···O(17)···H(2) 98.8(9).

To find out, if there is a comparable structural diversity as found for diamines,[6] we have reacted diols with $(Ph_2SiO)_8[Al(O)OH]_4$. We have succeeded to obtain crystalline solids on using 1,6-hexane diol and 1,4-cyclohexane diol which form the adducts **3** and **4**. The structures of these compounds are depicted in Figure 4 and Figure 5. As may be seen from these pictures all OH groups of $(Ph_2SiO)_8[Al(O)OH]_4$ are engaged in hydrogen bonding to the OH functions. Although alcohols in general are much weaker Lewis bases than primary amines, they nevertheless act as such vs. the OH groups of $(Ph_2SiO)_8[Al(O)OH]_4$.[13] Both structures form coordination polymers in the crystal, interestingly in quite different ways.

In the crystal structure of **3** (the $(Ph_2SiO)_8[Al(O)OH]_4$ polycycles have crystallographic C_2 point symmetry) the 1,6-hexane diol is bridging with its two OH groups either two different Al-O(H)-Al in the same molecule [O(2) and O(2')] or two different in neighboring molecules [O(3) and O(3")](see Figure 4). In the first case a O–H··O(H)–$(CH_2)_6$–(H)O··H–O loop is created, which is intersected by the twofold axis, while in the second case a connection arises to a proximate second polycycle (the sixfold carbon chain is intersected by an inversion center). In such a way an one dimensional hydrogen bridged chain is formed, which (due to the inversion center) has the connected $(Ph_2SiO)_8[Al(O)OH]_4$ polycycles on opposite sites of the polymeric chain (see also Figure 4); benzene and toluene molecules fill up the lattice. There is a very similar structure to **3**, when in the place of 1,6-hexane diol the diamine 1,4-butane diamine is used: again a compound of 1:2 ratio between the alumo-oxy polycycle and the bidentate base, $(Ph_2SiO)_8[Al(O)OH]_4 \cdot 2\ H_2N\text{-}(CH_2)_4\text{-}NH_2$, is formed with an O-H··N(H_2)-$(CH_2)_4$-(H_2)N··H-O intramolecular loop and an intermolecular connection between molecules forming a one-dimensional polymer.[6]

The mean Al–O bond length within the eight-membered ring of **3** is 1.796(3) Å, which is in the range of the diethyl ether adduct of $(Ph_2SiO)_8[Al(O)OH]_4$ (1.796 Å)[7] although the proton affinity of alcohols (ca. 800 kJ·mol^{-1}) is normally somewhat lower than that of ethers (ca. 825 kJ·mol^{-1}).[13] Another remarkable feature are the almost similar spacings of the oxygen atoms engaged in hydrogen bridging (see Figure 4), independently of the hexane diol either forming a chain or a loop. The O···O spacings in **3** [mean: 2.618(1) Å] are even smaller than in molecule **2** [mean 2.646(15) Å]. The Al–O(Si) [mean: 1.707(4) Å] and Si–O(Si) [mean: 1.622(4) Å] bonds in the alumo-oxo-siloxy polycycle are in the usual range.[6]

The change from open chain into a cyclic diol has a tremendous effect on the structure of the adduct with $(Ph_2SiO)_8[Al(O)OH]_4$. In Figure 5 the adduct with 1,4-cyclohexane diol **4** is depicted showing that each of the diols is coordinated with one functional OH end at the polycycle while the other is participating in a fourfold O···H–O hydrogen bridge.

As highlighted in Figure 5 the four hydroxy groups forming the quadruple hydrogen bridge come from different molecules **4**: therefore, a three-dimensional connection of molecules is

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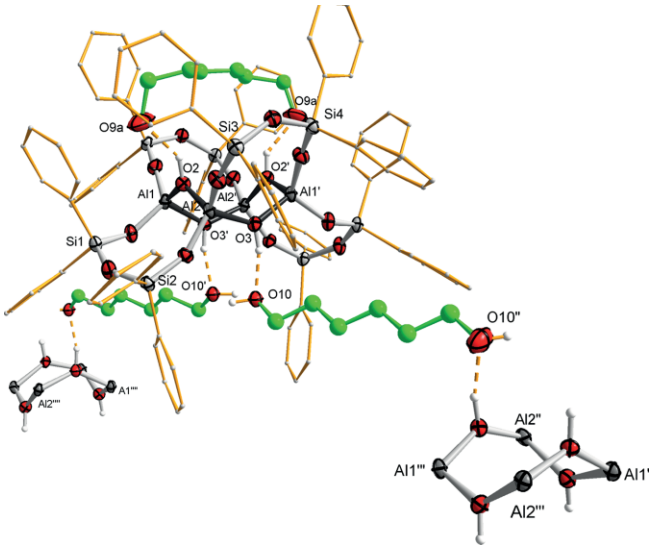

Figure 4. A cutout of the crystal structure of $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}2HO–CH_2(CH_2)_4CH_2–OH$ (**3**) with thermal ellipsoids (50 %) at Si, Al, O and ball and stick models for other atoms omitting benzene and toluene molecules incorporated in the crystal. The bonds and the carbon atoms within the 1,6-hexane diol molecules are in green. From the two symmetry related molecules (" and ' ") only the $Al_4[O(H)]_4$ rings are drawn. Some pertinent bond lengths /Å and angles /°: Al(1)–O(2) 1.801(2), Al(2)–O(2) 1.792(2), Al(2)–O(3) 1.802(2), Al(1')–O(3) 1.792(2); Al(2)–O(2)–Al(1) 127.1(2), Al(2)–O(3)–Al(1') 129.9(2). Hydrogen bonding: O(2)···O(9a) 2.620(5), O(3)···O(10) 2.617(5); O(9a)···H(1)–O(2) 142.0(3), O(10)···H(2)–O(3) 166.9(3).

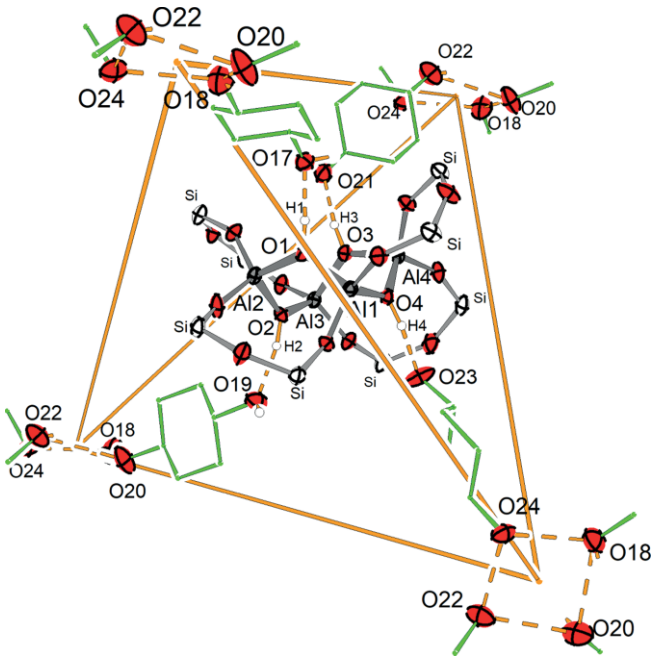

Figure 5. A cutout of the crystal structure of $(Ph_2SiO)_8[Al(O)OH]_4{\cdot}4HO–CH(CH_2CH_2)_2CH–OH$ (**4**) with thermal ellipsoids (50 %) at Si, Al, O and ball and stick models for other atoms. The three space filling toluene molecules are not drawn. The phenyl groups at the silicon atoms have been omitted for clarity. The bonds and the carbon atoms within the 1,4-cyclohexane diol molecules are in green. The centers of the four terminal OH groups forming four hydrogen bridged assemblies around the molecule are connected through lines which have a mean distance of 17.0(8) Å. Some pertinent bond lengths /Å and angles /°: Al(1)–O(4) 1.796(3), Al(1)–O(1) 1.797(3), Al(2)–O(1) 1.794(3), Al(2)–O(2) 1.795(3), Al(3)–O(2) 1.799(3), Al(3)–O(3) 1.803(3), Al(4)–O(4) 1.799(3), Al(4)–O(3) 1.801(3), mean: Al–O(Si) 1.707(6), Si–O(Al) 1.606(6), Si–O(Si) 1.632(6); Al(2)–O(1)–Al(1) 125.4(2), Al(2)–O(2)–Al(3) 125.9(2), Al(4)–O(3)–Al(3) 126.0(2), Al(1)–O(4)–Al(4) 125.6(2). Hydrogen bonding: O(1)···O(17) 2.604(6), O(2)···O(19) 2.656(7), O(3)···O(21) 2.651(6), O(4)···O(23) 2.556(7), O(18)···O(20) 2.765(4), O(20)···O(22) 2.797(4), O(22)···O(24) 2.753(4), O(24)···O(18) 2.740(4); O(17)···H(1)–O(1) 174.1(4), O(19)···H(2)–O(2) 164.2(5), O(21)···H(3)–O(3) 170.7(4), O(23)···H(4)–O(4) 165.9(5).

formed which follows very roughly a cubic closed packing arrangement. If the middle of the four alcohol groups is taken as fixpoint, the mean distance between these points is 17.0(8) Å (see lines in Figure 5).

The mean Al–O distance within the eight-membered Al_4O_4 ring in **4** is with 1.798(2) Å almost equal to the corresponding bond length in **3** [1.796(3) Å] as expected, both compounds displaying the same functional group. The O···O spacings within the O–H···O bridges in **4** starting from oxygen atoms O(1–4) [2.62(5) Å] are distinctly shorter than those between the alcohol groups O(18), O(20), O(22) and O(24) [2.764(7) Å] which has to be attributed to the higher acidity of the hydrogen atoms in aluminum bonded OH groups. Contrarily to the adaptivity and flexibility of hexane diol to bind intra- and intermolecularly to $(Ph_2SiO)_8[Al(O)OH]_4$ as found in **3**, the cyclohexane diol is structurally more rigid and the distance between the two alcohol groups is shorter, which hampers an intramolecular hydrogen binding in **4**.

Whereas in all adducts **1–4** the central polycycle $(Ph_2SiO)_8[Al(O)OH]_4$ remains chemically and structurally unchanged, when the bases interact with the OH groups of the aluminum-oxygen ring, this is not the case, when lysine is used in the reaction with $(Ph_2SiO)_8[Al(O)OH]_4$ (see Scheme 2). Two processes can be formally stated: (1) the amino acid lysine is transformed to 3-amino-2-azepanone, and (2) the alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$ loses water and presumably the disilanol $HO–Si(Ph)_2OSi(Ph)_2–OH$ and is rearranged to $(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2$ by incorporation of two 3-amino-2-azepanone molecules as ligands to aluminum atoms. Two further 3-amino-2-azepanone molecules are bonded through N–H···N and O–H···O hydrogen bridges finally forming **5**. In Figure 6 a global view of the molecular structure of **5** is shown, while the inner part of the molecule is depicted in Figure 7. The molecule **5** has C_i point symmetry and 6 further THF molecules are incorporated in the crystal. Transformations of the alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$ with loss of water giving formally higher condensed aluminum oxide/hydroxides like in **5** have been observed before.[14–16] Also change of the central $Al_4[O(H)]_4$ structure of $(Ph_2SiO)_8[Al(O)OH]_4$ by rearrangement of the Al–O(OH) skeleton have been encountered,[6,17] especially when very small bases like water or ammonia are used.[6,18,19]

Until now only the base NH_3 has been found to bind directly to aluminum instead of coordinating to the protonic hydrogen atoms of the central $Al_4[O(H)]_4$ ring of $(Ph_2SiO)_8[Al(O)OH]_4$.[19] In compound **5** we find for the first time a base which is chelating Al atoms of the central skeleton of **5** through the amino nitrogen atom [N(1)] and the carbonyl oxygen atom [O(14)]

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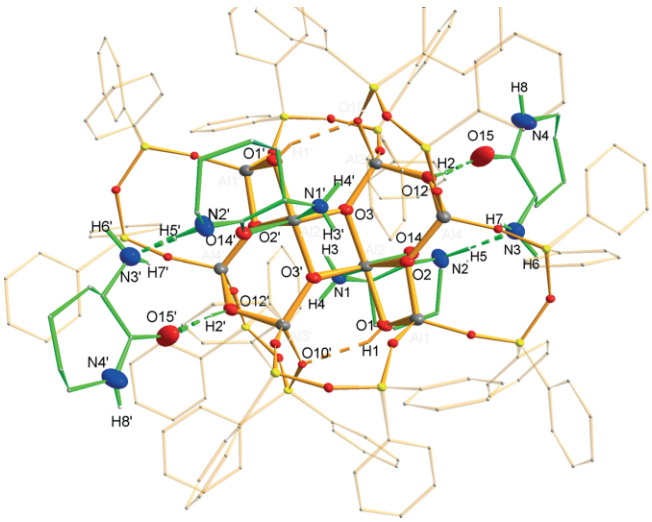

Figure 6. Part of the crystal structure of $(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2{\cdot}4C_6H_{12}N_2O{\cdot}6(CH_2)_4O$ (**5**) with thermal ellipsoids (50 %) at the central Al, O and the N/O atoms of the four 3-amino-2-azepanone molecules. The silicon and their oxygen atoms bonded to them have been reduced in size, the phenyl groups are simplified and made more transparent while the six THF molecules have been omitted for clarity. The bonds and the carbon atoms within the 3-amino-2-azepanone molecules are in green. The hydrogen bridges have a plain and a dotted line. Some pertinent bond lengths /Å and angles /°: Al(1)–O(4) 1.712(3), Al(1)–O(7) 1.715(3), Al(1)–O(2) 1.774(3), Al(1)–O(1) 1.790(4), Al(2)–O(3) 1.859(3), Al(2)–O(3') 1.859(3), Al(2)–O(2) 1.912(3), Al(2)–O(14) 1.913(3), Al(2)–O(1) 1.935(3), Al(2)–N(1) 2.080(4), Al(3)–O(9) 1.707(3), Al(3)–O(3) 1.739(3), Al(3)–O(10) 1.761(3), Al(3)–O(12) 1.793(3), Al(4)–O(6) 1.712(3), Al(4)–O(13) 1.720(3), Al(4)–O(2) 1.753(3), Al(4)–O(12) 1.793(3); O(3)–Al(2)–O(3') 82.5(1), O(3)–Al(2)–O(2) 102.7(1), O(3')–Al(2)–O(2) 96.4(1), O(3)–Al(2)–O(14) 170.3(2), O(3')–Al(2)–O(14) 94.6(1), O(2)–Al(2)–O(14) 86.8(1), O(3)–Al(2)–O(1) 92.8(1), O(3')–Al(2)–O(1) 172.9(1), O(2)–Al(2)–O(1) 79.5(1), O(14)–Al(2)–O(1) 91.0(1), O(3)–Al(2)–N(1) 92.4(1), O(3')–Al(2)–N(1) 94.3(2), O(2)–Al(2)–N(1) 162.5(2), O(14)–Al(2)–N(1) 78.6(1), O(1)–Al(2)–N(1) 91.1(1), Al(1)–O(1)–Al(2) 95.4(1), Al(4)–O(2)–Al(1) 129.6(2), Al(4)–O(2)–Al(2) 124.5(1), Al(1)–O(2)–Al(2) 96.7(1), Al(3)–O(3)–Al(2) 133.3(2), Al(3)–O(3)–Al(2') 126.7(2), Al(2)–O(3)–Al(2') 97.5(1). More details of the inner skeleton and hydrogen bridges see Figure 7!.

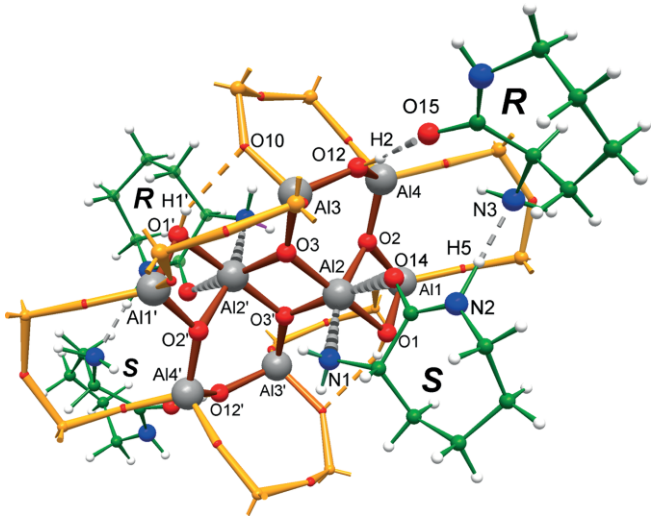

Figure 7. The inner part of $(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2{\cdot}4C_6H_{12}N_2O{\cdot}6(CH_2)_4O$ (**5**) as ball and stick model. The four 3-amino-2-azepanone molecules in green (marked with their corresponding chirality) are completely shown, whereas the –O–$SiPh_2$–O–$SiPh_2$–O– ligands are represented without the phenyl groups and in a simplified fashion. The hydrogen bonding may be characterized as follows: N(2)···N(3) 2.887(7), O(12)···O(15) 2.576(6), O(1')···O(10) 2.837(6); N(3)···H(5)–N(2) 176.1(4), O(15)···H(2)–O(12) 173.2(5), O(10)···H(1')–O(1') 153.4(4).

of the 3-amino-2-azepanone. The central unit of **5**, which is depicted in a simplified way in Figure 7, consists of eight aluminum atoms which are hold together by four oxygen atoms [O(2), O(3), O(2'), O(3')]. These oxygen atoms are in almost planar trigonal aluminum environments [sum of angles around O(2): 350.9(2) °, around O(3): 357.5(2)°].

Four hydroxy groups [O(1), O(12), O(1'), O(12')] further connect the aluminum atoms assembled by oxygen atoms in such a way, that either a four-membered Al_2O_2 [Al(1), O(1), Al(2), O(2)] or six-membered Al_3O_3 [Al(2), O(3), Al(3), O(12), Al(4), O(2)] ring is formed. This $Al_8O_4(OH)_4$ molecule center is wrapped up by six –O–$Si(Ph)_2$–O–$Si(Ph)_2$–O– chains, either connecting aluminum atoms which are separated by one oxygen atom in the usual way forming the $Si_2Al_2O_4$ eight-membered rings, or in a novel linkage type. Here, the siloxane chain spans over two aluminum atoms [Al(1), Al(3')] which are linked to a O–Al–O unit [O(1), Al(2), O(3')] creating a ten membered $Al_3O_5Si_2$ cycle. The aluminum atoms Al(2) and Al(2') are almost octahedrally coordinated by five oxygen and one nitrogen atoms while the other aluminum atoms are in distorted tetrahedral oxygen environments (see caption of Figure 6). The coordination octahedra around Al(2) and Al(2'), are sharing one common edge [O(3),O(3')], and form further edges with the tetrahedra around Al(1) and Al(1'). The coordination tetrahedra around Al(3) and Al(4) are connected to the octahedra through corners [O(2) and O(3)].

As already mentioned one of the two symmetrically different 3-amino-2-azepanone molecules is forming a chelate to aluminum Al(2) with the O(14)–Al(2) bond length distinctly shorter then found for the N(1)–Al(2) (see caption Figure 6!). The O(14)–Al(2) bond length compares well with the other Al(2)–O(1, 2, 3, 3') contacts which have a mean value of 1.89(2) Å. The second 3-amino-2-azepanone is bonded to the first by a N(2)–H(5)···N(3) hydrogen bridge and connects further to the OH group of oxygen atom O(12) through the atom configuration O(15)···H(2)–O(12). This O···O bridge seems to be much stronger than the N···N bridge looking at the distances (caption of Figure 7). There is a third hydrogen bridge within the molecule between an OH group of the central Al/O assembly and the oxygen atom of an alumo-oxo-silyl chain [O(10)···H(1')–O(1')]. Such bridges are scarce, because of the low basicity of the Al–O–Si arrangement, and have been found in compounds with a high amount of hydroxyl groups like $(Ph_2SiO)_{12}[Al(O)OH]_6[Al(OH)_3]{\cdot}3OEt_2$.[18] The two symmetrically different 3-amino-2-azepanones are stereo isomers and can be assigned to *R* and *S* as shown in Figure 7.

The Al–O(Al) bonds in **5** reflect nicely the coordination numbers at the aluminum atoms, as they are short, when they belong to tetrahedrally coordinated aluminum atoms [mean: 1.77(1) Å], and are long at aluminum atom Al(2) which is in

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an octahedral environment [mean: 1.90(1) Å]. The bond lengths Al–O of oxygen atoms which are further linked to silicon [mean: 1.713(5) Å] are, as found for the other compounds in this article, shorter than those of oxygen atoms exclusively linked to aluminum. As already mentioned, the by 0.26 Å shorter O(15)···O(12) distance compared to O(1')···O(10) (compare caption of Figure 7) is most probably due to the low basicity of the O(10) atom which is involved in a bond to silicon. Nevertheless, the Al(3)–O(10) bond is elongated compared to the other Al–O(Si) bonds by 0.048 Å as consequence of the O(10)···H(1)–O(1) bridge.

Conclusions

The flexibility and adaptability of the cyclic alumosiloxane $(Ph_2SiO)_8[Al(O)OH]_4$ to coordinate through the hydroxy groups of the central ring to different bases has again been demonstrated with the structure analyses of compounds **1–4**. Pyrazine (**1**) and ethyl acetate (**2**) form 1:3 adducts, but only in **2** all hydroxy groups are engaged in bonding to the bases: here we have characterized for the first time within the alumosiloxane adducts a single carbonyl oxygen atom connecting two hydroxy groups on the same side of the $Al_4[O(H)]_4$ ring forming an O–H···O···H-O double hydrogen bridge. The 1:2 stoichiometry of $(Ph_2SiO)_8[Al(O)OH]_4$ and 1,6-hexane diol in **3** can be traced back to the intra- and intermolecular bonding of the diol, whereas in **4** the four 1,4-cyclohexane diols bind with one end to the hydroxy groups of the alumosiloxane and with the other to three more tails of the diols, ending up in a quadruple hydrogen bridged entity. The alcohol agglomeration causes a three-dimensional connection between the molecular centers, which has a great similarity to a cubic close packing of equal spheres.

The adduct **5** is the first example of an amino acid interacting with $(Ph_2SiO)_8[Al(O)OH]_4$. During the reaction with lysine not only the amino acid is transformed to 3-amino-2-azepanone but also part of the Al(OH) groups in the alumosiloxane are converted into Al-O-Al bonds. As a result, a more condensed Al/O-polycycle is formed. Furthermore one of two 3-amino-2-azepanones is chelating one of the aluminum atoms through the carbonyl oxygen atom and the NH_2-substituent on the ring of the 3-amino-2-azepanone. The second 3-amino-2-azepanone molecule is attached through hydrogen bridges in the usual way.

Although it is not possible to transfer molecular results to solid surfaces in a 1 : 1 fashion, it is nevertheless remarkable that amino acids (or derivatives) may not only bind to Al_2O_3/OAlOH surfaces through hydrogen bridges, but could also directly bind to aluminum. This could be a valuable hint for alumina surface reactions of peptides (see also references[1–3,10,11]).

Experimental Section

All manipulations were performed in a nitrogen atmosphere under strict exclusion of water and air. Solvents were purified prior to use by distillation and were kept over sodium wire. NMR spectra were obtained with Bruker AC200F/AC200P and FT-IR with a Varian 2000. The data sampling for single-crystal X-ray diffraction analyses was performed with a Bruker X8 Apex II CCD using Mo-K_α radiation. The structures were solved and refined using the SHELX-system and are graphically represented using the *Diamond* program.[20,21]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2033704 (**1**), CCDC-2033705 (**2**), CCDC-2033706 (**3**), CCDC-2033707 (**4**), and CCDC-2033708 (**5**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

$(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3N(C_2H_2)_2N{\cdot}C_6H_5$-$CH_3$ (1): To a suspension of 1.00 g (0.47 mmol) $(Ph_2SiO)_8[AlO(OH)]_4{\cdot}4\,Et_2O$ in diethyl ether (20 mL) a solution of 0.15 g (1.89 mmol) pyrazine in diethyl ether (10 mL) is added slowly at room temperature generating a clear solution. After few minutes, a colorless precipitate forms which increases on further stirring. After 22 h 0.62 g (0.29 mmol) of colorless crystals of **1** (61 %) have been obtained by filtration. They dissolve in toluene and tetrahydrofuran from which they can be recrystallized. $C_{108}H_{96}N_6O_{16}Si_8Al_4{\cdot}C_7H_8$ (2158.68): calcd. C 63.99, H 4.86, N 3.89 %; found C 62.21, H 4.94, N 3.82 %. **^{1}H NMR** (THF)**:** δ = 2.17 (3.0, s, C_6H_5-CH_3), 6.8–7.2 (53.0, m, C_6H_5(*m/p*)/C_6H_5-CH_3), 7.4–7.5 (32.0, m, C_6H_5(*o*)), 8.28 (12.0, s, $C_4H_4N_2$). **^{13}C NMR** (THF): δ = 21.0 (C_6H_5-CH_3), 125.5 (*p*-C_6H_5-CH_3), 127.4–127.5 (*m*-C_6H_5), 128.4 (*m*-C_6H_5-CH_3), 129.2 (*o*-C_6H_5-CH_3), 129.2/129.3 (*p*-C_6H_5), 134.8–134.9 (*o*-C_6H_5), 138.5–139.0 (Si-C_6H_5), 137.9 (CH_3–C_6H_5), 145.4 (NC_4H_4N). **^{29}Si NMR** (THF): δ = –45.8. **FT-IR**: $\tilde{\nu}$ = 3608 (OH, w), 3314 (OH, br/w), 3071, 3046, 3018, 3000 (CH) cm^{-1}. **X-ray data**: Triclinic, $P\bar{1}$, a = 14.8724(6), b = 15.0963(6), c = 26.879(9) Å, α = 77.359(2), β = 82.902(2), γ = 74.072(2)°, V = 5649.5(4) Å^3, Z = 2. Measuring temperature: 153 K. Structure refinement: 34429 reflections (R(int) = 0.0272); θ (°) = 1.43 to 30.53; completeness to θ = 25.242: 99.6 %; max. and min. transmission: 0.746 and 0.699); refinement method: full-matrix least-squares on F^2; 1352 parameters (170 restrains); final R indices [$I > 2\sigma(I)$]: R_1 = 0.0448, wR_2 = 0.1118; largest diff. peak and hole: [e·Å^{-3}] 0.913 and –0.522. The phenyl substituent C(55)–C(60) is disordered causing B-level alerts in the checkcif-file. The O(2)–H(2) bond has no base acceptor.

$(Ph_2SiO)_8[Al(O)OH]_4{\cdot}3H_3CC(O)OC_2H_5$ (2): To 1.254 g (0.591 mmol) $(Ph_2SiO)_8[AlO(OH)]_4{\cdot}4\,Et_2O$ dissolved in toluene (15 mL) a solution of 0.23 mL (2.363 mmol) ethyl acetate (freshly distilled before use) in toluene (10 mL) is added dropwise at room temperature. After 18h of stirring the reaction mixture is reduced to 1/3 by condensation of the solvents into cold traps. On standing crystallization begins yielding 0.84 g (0.40 mmol) of **2** (68 %). $C_{108}H_{107}O_{22}Si_8Al_4$ (2089.58): calcd. C 62.08, H 5.16 %; found C 57.85, H 4.97 % (moisture sensitivity). **^{1}H NMR** (C_6H_6)**:** δ = 0.56 (9.0, t, $CH_3COOCH_2CH_3$), 1.12 (9.0, s, $CH_3COOCH_2CH_3$), 3,43 (6.0, q, $CH_3COOCH_2CH_3$) 7.7–7.98 (32.0, m, C_6H_5(*o*)). **^{13}C NMR** (C_6H_6): δ = 13.3 ($CH_3COOCH_2CH_3$),, 127.4–127.5 (*m*-C_6H_5), 128.4 (*m*-C_6H_5-CH_3), 129.2 (*o*-C_6H_5-CH_3), 129.2/129.3 (*p*-C_6H_5), 134.8–134.9 (*o*-C_6H_5), 138.5–139.0 (Si-C_6H_5), 137.9 (CH_3–C_6H_5). **^{29}Si NMR** (C_6H_6): δ = –44.3. **FT-IR**: $\tilde{\nu}$ = 3606 (OH, w), 3534 (OH), 3357 (OH, br/w), 3312(OH, br), 3070, 3048, 3003, 2910 (CH), 1697 (C=O), 1666 (C=O) cm^{-1}. **X-ray data**: Monoclinic, $P2_1/n$, a = 27.1062(9), b = 15.0407(5), c = 28.011(1) Å, β = 106.771(2), V = 10934.1(6) Å^3, Z = 4. Measuring temperature: 122 K. Structure refinement: 30784 reflections (R(int) = 0.0429); θ (°) = 1.24 to 29.86; completeness to θ = 25.242°: 100.0 %; max. and min. transmission: 0.746 and 0.670); refinement method: full-matrix least-squares on F^2; 1352 parameters (18 restrains); final R indices [$I > 2\sigma(I)$]: R_1 = 0.0563, wR_2 = 0.1267; largest diff. peak and hole: [e·Å^{-3}] 0.883 and –0.916.

$(Ph_2SiO)_8[AlO(OH)]_4{\cdot}2(HO$-$(CH_2)_6$-$OH){\cdot}C_6H_6{\cdot}C_7H_8$ (3): To 0.899g (0.424 mmol) $(Ph_2SiO)_8[AlO(OH)]_4{\cdot}4\,Et_2O$ in benzene (10mL) are added

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dropwise a solution of 150 mg (1.271 mmol) 1,6-hexane diol in toluene (5 mL) at room temperature. After stirring for 12h the formed colorless precipitate is separated by filtration. The solid dissolves in benzene at around 60 °C from which it can be crystallized as **2**: 0.84g (0.354 mmol) (83 %). $C_{121}H_{126}Al_4O_{20}Si_8$ (2232.85): calcd. C 65.09, H 5.69 ; found C 65.20, H 6.05 %. **^{1}H NMR** (THF)**:** CH_2-region masked by solvents, δ = 6.9–7.2 (m, *m,p*-C_6H_5), 7.4–7.6 (m, *o*-C_6H_5). **^{13}C NMR** (THF): δ = 26.69 ($HOCH_2CH_2CH_2)_2$), 33.70 ($HOCH_2CH_2CH_2)_2$), 62.13 ($HOCH_2CH_2CH_2)_2$),127.3–127.5 (*m*-C_6H_5), 129.2/129.3 (*p*-C_6H_5), 134.0–135.1 (*o*-C_6H_5), 138.5/139.0 (Si-C_6H_5). **^{29}Si NMR** (THF): δ = –45.7. **FT-IR**: $\tilde{\nu}$ = 3557 (OH), 3066, 3048, 3018, 3000, 2941, 2908, 2890, 2859 (CH) cm^{-1}. **X-ray data**: Monoclinic, *C*2/*c*, *a* = 26.360(4), *b* = 19.766(4), *c* = 22.737(5) Å, β = 92.31(1)°, *V* = 11837(4) Å^3, *Z* = 4. Measuring temperature: 293 K. Structure refinement: 13078 reflections (*R*(int) = 0.14); θ (°) = 1.55 to 27.48; completeness to θ = 25.242°: 99.9 %; refinement method: full-matrix least-squares on F^2; 661 parameters (61 restrains); final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.060, wR_2 = 0.1334; largest diff. peak and hole: [e·Å^{-3}] 0.752 and –0.51.

$(Ph_2SiO)_8[AlO(OH)]_4$·4(HO)CH$(CH_2)_4$CH(OH)·3C_6H_5-CH_3 (4): To 0.21 g (1.80 mmol) 1,4-cyclohexane diol in toluene (10 mL) a solution of 0.95 g (0.45 mmol) $(Ph_2SiO)_8[AlO(OH)]_4$·4 Et_2O in toluene (10 mL) is added dropwise. The mixture is stirred for 5 days at ambient temperature forming a colorless precipitate, which is separated by filtration. The precipitate is kept under vacuum (10^{-3} atm) for 2h (separating volatiles in a cold trap) and redissolved in warm toluene (5 mL) from which 0.25 g (0.10 mmol) crystals of **4** form (22 %). $C_{141}H_{156}O_{24}Si_8Al_4$ (2567.30): calcd. C 65.69, H 6.12 %, found C 66.33. H 6.76 %. **^{1}H NMR** (THF): δ = 1.00–1.18 (32.0, m, (HO)CH(CH_2)$_4$CH(OH)), 2.15 (9.0, s, (C_6H_5)CH_3), 6,84–7,18 (63.0, m, *m*/*p*-C_6H_5)/C_6H_5-CH_3), 7.35–7.52 (32.0, m, *o*-C_6H_5). **^{13}C NMR** (THF): δ = 21.0 (C_6H_5-CH_3), 33.6 [(HO)CH(CH_2)$_4$CH(OH)], 69.2 [(HO)$CH(CH_2)_4CH$(OH)], 125.6 [*p*-(C_6H_5)CH_3], 127.5 (*m*-C_6H_5), 128.4 [*m*-(C_6H_5)CH_3], 129.2 [*o*-(C_6H_5)CH_3], 129.2 (*p*-C_6H_5), 134.9 (o-C_6H_5), 137.9 (CH_3–C_6H_5), 138.6 (Si-*C*), 139.0 (Si-*C*). **^{29}Si NMR** (THF): δ = –45.8. **FT-IR**: $\tilde{\nu}$ = 3299 (br., OH), 3047, 3003, 2940, 2862 (CH) cm^{-1}. **X-ray data**: Monoclinic, *Cc*, *a* = 29.205(4), *b* = 17.228(4), *c* = 28.657(5) Å, β = 107.54(1), *V* = 13748(5) Å^3, *Z* = 4. Measuring temperature: 120 K. Structure refinement: 40210 reflections (*R*(int) = 0.0516); θ (°) = 1.39 to 32.92; completeness to θ = 25.242°: 98.5 %; max. and min. transmission: 0.746 and 0.693); refinement method: full-matrix least-squares on F^2; 1595 parameters (8 restrains); final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0573, wR_2 = 0.1358; largest diff. peak and hole: [e·Å^{-3}] 0.771 and –0.387. High shift errors due to methyl groups of toluene, which have local disorder, and H···H small contacts due to imprecision of hydrogen positions on O–H groups cause some B level alerts in the checkcif file. All O–H···O contacts have been geometrically checked.

$(Ph_2SiO)_{12}[Al(O)OH]_4[Al_2O_3]_2$·4$C_6H_{12}N_2O$·6$(CH_2)_4O$ (5): To a suspension of 0.45 g (2.74 mmol) R,S-lysine in toluene (70 mL), heated until the solvent is boiling and cooled down again, a solution of 1.46 g (0.69 mmol) $(Ph_2SiO)_8[AlO(OH)]_4$·4 Et_2O in toluene (30 mL) is added dropwise, on which the suspension is clearing up. Further 20h heating under reflux leads to a completely transparent solution. The solvent is condensed into cold traps (10^{-2} mbar) resulting in 1.63 g (0.44 mmol) of the yellow solid **5** (64 %), which can be redissolved in THF and crystallized on standing. $C_{192}H_{220}Al_8N_8O_{36}Si_{12}$ (3768.67): calcd. C 61.19, H 5.88, N 2.97 %, found C 59.38, H 6.16, N 3.81 %. **^{1}H NMR** (toluene): δ = 0.873–0.998 (m. $C_6H_{12}N_2O$), 1.00–1.18 (m, $C_6H_{12}N_2O$), 1.24–1.53 (m, $C_6H_{12}N_2O$), 2.92–3.09 (m, $C_6H_{12}N_2O$), 7.56–8.27 (m, C_6H_5). **^{13}C NMR** (toluene): δ = 23.2 [$C_6H_{12}N_2O$ (C4)], 27.3–32.4 [several signals, $C_6H_{12}N_2O$ (C5)], 34.5 [$C_6H_{12}N_2O$ (C3)] 41.5 [$C_6H_{12}N_2O$ (C6)], 53.6 [$C_6H_{12}N_2O$ (C2)], 127.6/127.7 (*m*-C_6H_5), 129.8/130.1 (*p*-C_6H_5), 134.4–136.1 (*o*-C_6H_5), 139.4 –141.0 (Si-*C*), 179.1 [$C_6H_{12}N_2O$ (C1)]. **^{29}Si NMR** (THF): δ = –38, –47. **FT-IR**: $\tilde{\nu}$ = 3663 (OH), 3521 (OH), 3333 (NH), 3046, 300, 2926, 2854 (CH), 1651 (C=O) cm^{-1}. **X-ray data**: Monoclinic, $P2_1/n$, *a* = 18.559(2), *b* = 24.169(3), *c* = 21.627(5) Å, β = 97.69(1), *V* = 9613(2) Å^3, *Z* = 2. Measuring temperature: 132 K. Structure refinement: 22883 reflections (*R*(int) = 0.154); θ (°) = 1.27 to 27.92; completeness θ = 25.242°: 100.0 %; refinement method: full-matrix least-squares on F^2; 1170 parameters (49 restrains); final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0635, wR_2 = 0.1289; largest diff. peak and hole: [e·Å^{-3}] 0.684 and –0.562.

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References

[1] B. Love, *Biomaterials, A systems Approach to Engineering Concepts*, Academic Press, Cambridge, Mass. USA, **2017**, 185–204.
[2] E. P.Ivanova, K. Bazaka, R. J. Crawford, *New Functional Biomaterials for Medicine and Healthcare*, Woodhead Publishing, Cambridge, UK, **2014**.
[3] M. Veith, J. Lee, M. Martinez-Miró, C. Kaan Akkan, C. Dufloux, O. C. Aktas, *Chem. Soc. Rev.* **2012**, *41*, 5117.
[4] P. Thissen, G. Grundmeier, S. Wippermann, W. G. Schmidt, *Phys. Rev. B* **2009**, *80*, 245403.
[5] H. A. Al-Abadleh, V. H. Grassian, *Langmuir* **2003**, *19*, 344.
[6] M. Veith, *Adv. Organomet. Chem.* **2006**, *54*, 49.
[7] M. Veith, M. Jarczyk, V. Huch, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 117.
[8] M. Veith, D. Kolano, V. Huch, J. P. Sutter, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1922.
[9] M. Veith, M. Jarczyk, V. Huch, *Angew. Chem. Int. Ed.* **1998**, *37*, 105.
[10] K. Kiefer, G. Akpınar, A. Haidar, T. Ikier, C. Kaan Akkan, E. Akman, J. Lee, M. Martinez-Miró, E. Kaçar, A. Demir, M. Veith, D. Ural, M. Kasap, M. Kesmez, H. Abdul-Khaliq, C. Aktas, *RSC Adv.* **2016**, *6*, 17460.
[11] W. Metzger, B. Schwab, M. Martinez-Miró, S. Grad, A. Simpson, M. Veith, G. Wennemuth, V. Zaporojtchenko, S. Verrier, J. S. Hayes, M. Bubel, T. Pohlemann, M. Oberringer, C. Aktas, *J. Biomed. Nanotechnol.* **2014**, *10*, 831.
[12] A. Bladé-Font, *Tetrahedron Lett.* **1980**, *21*, 2443.
[13] E. Hunter, S. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
[14] M. Veith, F. Sahin, A. Rammo, V. Huch, *C. R. Chim.* **2009**, *12*, 1181.
[15] M. Veith, A. Rammo, V. Huch, J. Biegler, *Z. Anorg. Allg. Chem.* **2007**, *633*, 246.
[16] M. Veith, D. Kolano, T. Kirs, V. Huch, *J. Organomet. Chem.* **2010**, *695*, 1074.
[17] M. Veith, H. Hreleva-Caparotti, F. Sahin, V. Huch, *Z. Anorg. Allg. Chem.* **2014**, *640*, 863.
[18] M. Veith, M. Jarczyk, V. Huch, *Phosphor Sulfur Silicon* **1997**, *124–125*, 213.
[19] M. Veith, A. Rammo, M. Jarczyk, V. Huch, *Monatsh. Chem.* **1999**, *37*, 105.
[20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
[21] K. Brandenburg, *Program Diamond*, **2008**, Crystal Impact GbR, Bonn, Germany.

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