

Two new metal derivatives of the alumosiloxane [Ph₂SiO]₈[AlO(OH)]₄: [Ph₂SiO]₈[AlO₂(Na)]₄ · 5(THF) and [Ph₂SiO]₈[AlO(OH)]₂[AlO₂]₂[Zn(OH)]₂ · 2(OEt₂)

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Abstract

When the polycyclic alumosiloxane [Ph₂SiO]₈[AlO(OH)]₄ is allowed to react with either cyclopentadienyl sodium in tetrahydrofuran or with dimethyl zinc in diethyl ether the organic ligands on the metal elements are eliminated as cyclopentadiene or methane and the metals are bonded to oxygen atoms in the alumosiloxane forming [Ph₂SiO]₈[AlO₂(Na)]₄ · 5(THF) or [Ph₂SiO]₈[AlO(OH)]₂[AlO₂]₂[Zn(OH)]₂ · 2(OEt₂), respectively. X-ray structure determinations reveal that in the sodium derivative the original polycycle rests almost unchanged while in the zinc derivative the inner skeleton is rearranged.

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Keywords: Metal derivatives; Alumosiloxane; NMR; Crystal structure

1. Introduction

While alumosilicates and especially zeolites are well known for their use in catalysis, separation techniques (molecular sieves), water absorbers, nano-templates, scaffolds for three-dimensional construction, etc. [1–3], their molecular counterparts, which are often addressed as molecular alumosiloxanes, are less studied [4]. Nevertheless, they have also interesting properties as they combine the “solid state” properties of the inner AlSi_xO_y-skeletons with the solubility of the compounds in organic solvents and are therefore excellent candidates for molecular processing. We have in the past concentrated our efforts on compounds which are derived from siloxanes (R₂SiO)_n by substitution of (R₂SiO) entities by (HOAlO) units. The most prominent example of such a molecule is the tetrameric {(Ph₂SiO)₂[AlO(OH)]₂}₄ [5].

The alumosiloxane [Ph₂SiO]₈[AlO(OH)]₄ frequently reacts with bases like diethyl ether, tetrahydrofuran, triethylamine, pyridine to form adducts through hydrogen bonding using the acidic OH-groups in the molecule [5–8]. With diamines of the general formula H₂N–(CH₂)_n–NH₂ intra- and intermolecular adducts can be formed opening a whole family of supra-molecular chemistry [9,10]. Metal compounds like LiNH₂, LiPh or dicyclopentadienylegermanium or -tin can replace up to four acidic hydrogen atoms in [Ph₂SiO]₈[AlO(OH)]₄ to form molecular pseudo-alumosilicates like [Ph₂SiO]₈[AlO₂(Li)]₄, [Ph₂SiO]₈[AlO(OH)]₂[AlO₂]₂Ge or [Ph₂SiO]₈[AlO₂]₄(Sn)₂ [11,12]. We report here the syntheses and structures of two new metal derivatives, the metal being either sodium or zinc.

2. Syntheses and structures of

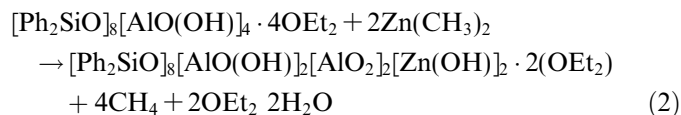
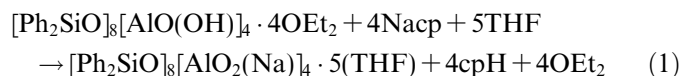
[Ph₂SiO]₈[AlO₂(Na)]₄ · 5(THF) and
[Ph₂SiO]₈[AlO(OH)]₂[AlO₂]₂[Zn(OH)]₂ · 2(OEt₂)

The etherate of alumosiloxane [Ph₂SiO]₈[AlO(OH)]₄ · 4OEt₂ is allowed to react either with sodium

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cyclopentadienide [13] in tetrahydrofuran or with dimethylzinc [14] in toluene using a 1:4 stoichiometry in the first case or a 1:2 stoichiometry in the second. Using sodium cyclopentadienide the progress of the reaction can be recognized by the change of the coloured solution from violet to colourless, while with dimethylzinc steady evolution of methane is observed. Both reactions are terminated by crystalline precipitations of the products (Eqs. (1) and (2))



The ^1H and ^{13}C NMR spectra of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ and $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ show besides the typical patterns due to the phenyl groups the signals for THF and diethyl ether revealing the coordinated bases. While in the ^{29}Si NMR solution spectrum of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ only one signal at 39.18 ppm is visible, the zinc-compound displays three signals (43.66, 44.68, 45.59 ppm) with intensities 2:1:1. In the solid, the spectrum of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ becomes more complex showing four broad resonance peaks (45.35, 47.56, 48.54, 49.16 ppm). Apparently in solution the dissymmetry of the solid is destroyed due to molecular motion within the molecule in which even the sodium atoms could be involved as may be concluded from the X-ray structure determination (see below). The IR-spec-

trum of single crystals of the sodium compound has no absorptions in the OH-region between 3600 and 3100 cm^{-1} , whereas the zinc-compound has weak absorption peaks at around 3400 cm^{-1} . The reaction pathway leading to $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ is not clear and the composition of the compound follows from elemental analysis and especially from the X-ray structure determination (see below). It might be possible that $\text{CH}_3\text{-Zn-OH}$ intermediates play an important part. Anyhow the yields of the sodium and the zinc compounds are almost quantitative, which rules out important water traces in the case of the zinc compound to come from water residues in the solvents.

Single crystals of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ and $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ have been obtained from concentrated solutions. Both compounds crystallize in the triclinic centro-symmetric space group $P\bar{1}$ with two or respectively one molecules per unit cell. More details of the structure determinations using X-ray diffraction are summarized in Table 1 and are deposited [21].

As with the lithium derivative $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OLi})]_4 \cdot 4\text{OEt}_2$ [6], all four hydrogen atoms of the central eight-membered ring of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_4$ are replaced in $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ (see also Fig. 1). The Al–O–Si-skeleton of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_4 \cdot 4\text{OEt}_2$ is influenced only little by the incorporation of sodium atoms, but the deviation from the S_4 symmetry is essentially higher compared to the lithium derivative. The compound $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ has the well-known central

Table 1

Crystal data of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ and $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$

Empirical formula	$\text{C}_{116}\text{H}_{120}\text{Al}_4\text{Na}_4\text{O}_{21}\text{Si}_8$	$\text{C}_{132}\text{H}_{134}\text{Al}_4\text{O}_{20}\text{Si}_8\text{Zn}_2$
Formula mass	2274.72	2503.78
Temperature (K)	210(2)	210(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 14.532(7)$ $\alpha = 90.5(1)$ $b = 16.791(8)$ $\beta = 93.1(1)$ $c = 24.78(3)$ $\gamma = 102.78(6)$	$a = 13.909(3)$ $\alpha = 64.33(3)$ $b = 15.666(3)$ $\beta = 73.92(3)$ $c = 17.529(4)$ $\gamma = 80.74(3)$
Volume (Å ³)	5886(7)	3304.2(12)
Z	2	1
D_{calc} (Mg/m ³)	1.284	1.258
Absorption coefficient (mm ⁻¹)	0.202	0.526
$F(000)$	2384	1310
Crystal size (mm)	0.52 × 0.33 × 0.25	0.63 × 0.5 × 0.3
θ Range for data collection (°)	1.85–23.90	2.64–23.92
Index ranges	$-16 \leq h \leq 16$, $-18 \leq k \leq 17$, $-27 \leq l \leq 27$	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	34571	20401
Independent reflections	16839 [$R_{\text{int}} = 0.0602$]	9543 [$R_{\text{int}} = 0.0529$]
Completeness to $\theta = 23.9^\circ$ (%)	92.2	93.1
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	16839/0/1359	9543/0/672
Goodness-of-fit on F^2	1.288	1.014
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.067$, $wR_2 = 0.164$	$R_1 = 0.051$, $wR_2 = 0.152$
R indices (all data)	$R_1 = 0.104$, $wR_2 = 0.176$	$R_1 = 0.060$, $wR_2 = 0.158$
Largest difference in peak and hole (e Å ⁻³)	0.66 and -0.592	0.815 and -0.506

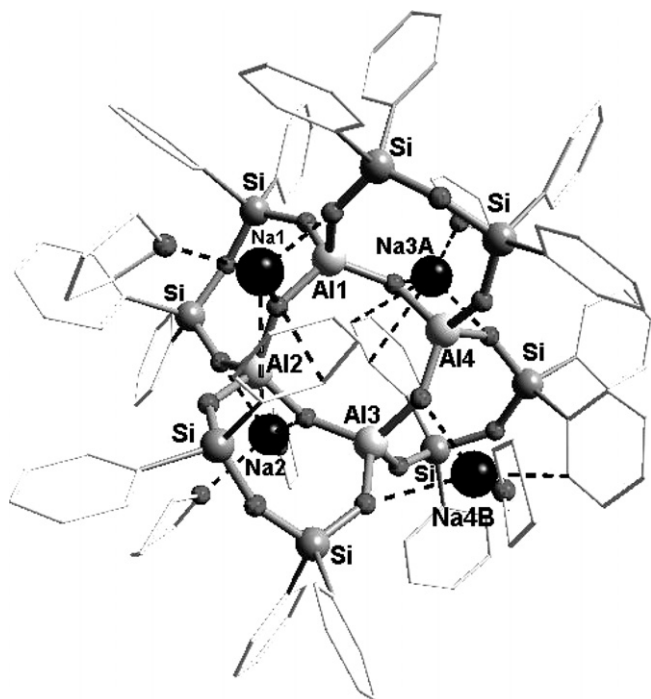


Fig. 1. Molecular structure of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ (the Ph groups of the siloxy rests and the donor molecules (THF) are only sketched for the sake of clarity. Only one of the two split-positions of sodium atoms Na3 and Na4 is drawn; compare also Fig. 2!).

cyclic Al_4O_4 structural unit which is completed by four annealed AlO_2Na four-membered rings. Compared to the lithium derivative, where a diethyl ether molecule is bound to each of the metal atoms through the oxygen atoms as a further ligand, THF is functioning in a similar way in compound $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$. But here, the four sodium atoms are differently coordinated. The Na(3)-atom is coordinated by three oxygen atoms, one of these taking its origin from a single THF molecule, resulting in a distorted trigonal coordination sphere, to which a further contact to the π -system of a neighbouring phenyl group has to be added (Na3A– πC 2.91(2)–2.99(2) Å; Na3B– πC 2.59(2) Å). Also the Na(1)-, Na(2)- and Na(4)-atoms have the coordination numbers 4 and occupy centres or distorted tetrahedra. The Na(2)-atom is interacting with two oxygen atoms of the aluminosiloxane chain and two oxygen atoms of two THF molecules. The atoms Na(1) and Na(4) are linked to two oxygen atoms of the aluminosiloxane chain and to one oxygen atom of a THF molecule. Furthermore these two atoms show short distances to two carbon atoms of adjacent diphenylsiloxy groups. For both sodium atoms the distances are in the range of bonding between sodium and aromatic π -systems (Na–aromatic π -system: 2.8–3.2 Å [15–19]; found: Na(1)–C 2.88(2) Å, Na(4A)– πC 3.12(2), Na(4B)– πC 2.66(2) Å). No spectral proof for the interaction between the sodium atoms and the aromatic π -systems has been obtained from the solid state ^{13}C -CP-MAS NMR spectrum of the compound $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ by a signal splitting of C-atoms of the phenyl group, due to

the quadrupole nucleus ^{23}Na because of resolution problems.

The asymmetric distribution of the ligands leads to the point symmetry C_1 in the molecule. The oxygen atoms in the AlO_2Na four-membered rings are almost trigonal planar surrounded by their rests and can be regarded as sp^2 -hybridized (the average angle sum of $\text{Al}-\text{O}-\text{Na} = 358.9(1)^\circ$). The mean Na–O-distance has a value of 2.339(6) Å and matches the regular Na–O bond length [20].

The average Al–O-distances (1.72(9) Å) are comparable with those of the lithium-alumino-siloxane $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{O-Li})]_4 \cdot 4\text{OEt}_2$ (average value of the Al–O bond length 1.729(4) Å) [6]. In Fig. 1, an almost symmetric location of the sodium atoms is displayed of compound $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$. Nevertheless this is only a crude image of the structure as the sodium atoms Na(3) and Na(4) are situated on split positions and are equally distributed between two crystallographic sites as may be deduced from Fig. 2.

These alternative positions are due to two interactions of different oxygen atoms of the aluminosiloxane chain. Apparently there is no great energy difference between these positions. This splitting may also be the consequence

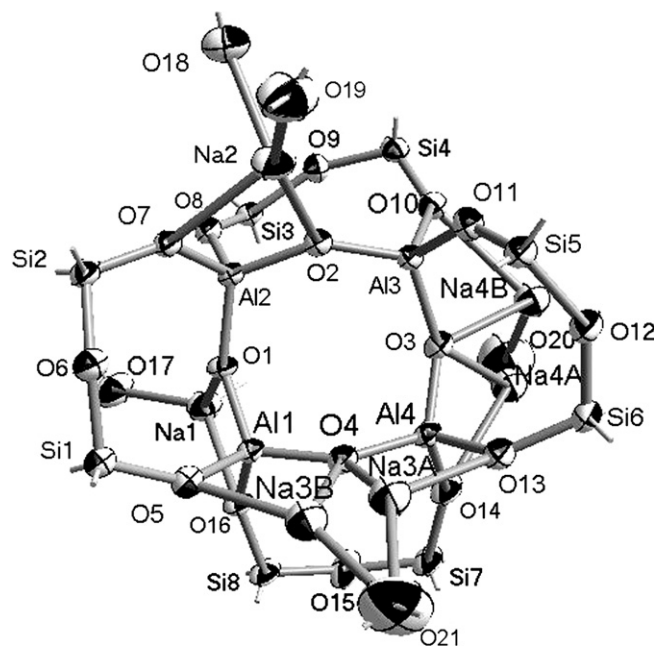


Fig. 2. Molecular structure of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$ indicating the splitting positions of the sodium atoms Na(3) and Na(4) and the Si–O–Al-skeleton (all carbon atoms are omitted for the sake of clarity; the anisotropic displacement ellipsoids are drawn with 50% probability). Selected distances (Å) and angles ($^\circ$): Al(1)–O(4) 1.725(3), Al(1)–O(1) 1.726(3), Al(2)–O(2) 1.725(3), Al(2)–O(1) 1.728(3), Al(3)–O(2) 1.731(3), Al(3)–O(3) 1.755(3), Al(4)–O(3) 1.718(4), Al(4)–O(4) 1.725(3), Na(1)–O(1) 2.273(4), Na(1)–O(16) 2.363(4), Na(2)–O(2) 2.340(4), Na(2)–O(7) 2.417(4), Na(4B)–O(3) 2.226(6), Na(4A)–O(3) 2.392(6), Na(3B)–O(4) 2.204(5), Na(3A)–O(4) 2.353(2), Na(3A)–O(5) 2.433(2), Na(4B)–O(10) 2.603(6), Na(3B)–O(13) 2.397(5), Na(4A)–O(14) 2.520(6), O(1)–Na(1)–O(16) 71.43(2), O(2)–Na(2)–O(7) 70.34(2), O(7)–Na(2)–O(18) 95.69(2), O(19)–Na(2)–O(7) 126.59(2), O(4)–Na(3A)–O(5) 71.8(4), O(4)–Na(3B)–O(13) 73.58(2), O(3)–Na(4A)–O(14) 70.54(2), O(3)–Na(4B)–O(10) 69.92(2).

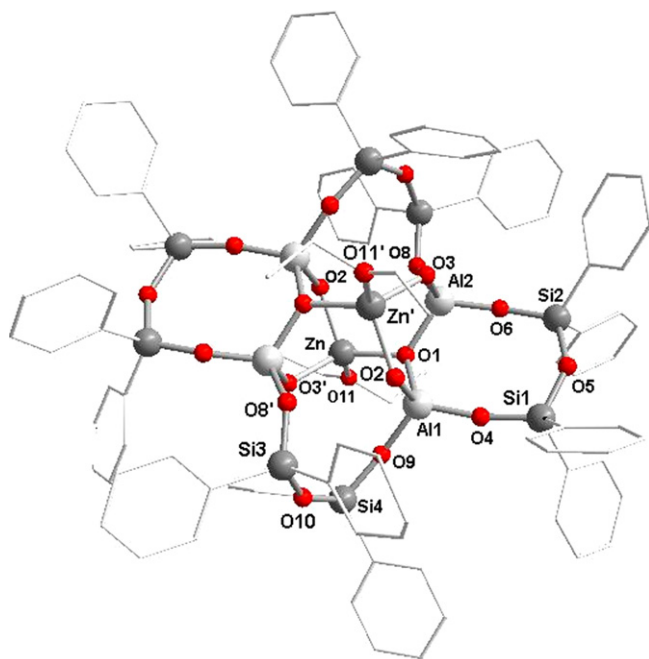


Fig. 3. Molecular structure of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{O}-\text{H})]_2 \cdot 2(\text{OEt}_2)$. Selected distances (Å) and angles ($^\circ$): Al(1)–O(1) 1.783(3), Al(1)–O(2) 1.800(3), Al(2)–O(1) 1.786(2), Al(2)–O(3) 1.797(3), Al(1)–O(4) 1.709(2), Al(1)–O(9) 1.731(2), Al(2)–O(6) 1.699(2), Al(2)–O(8) 1.736(3), Zn–O(3) 1.967(2), Zn–O(1) 1.949(2), Zn–O(2) 1.970(2), Zn–O(11) 1.998(3), O(3)–Zn–O(1) 116.9(1), O(3)–Zn–O(2) 101.2(1), O(1)–Zn–O(2) 110.7(1), O(3)–Zn–O(11) 111.2(1), O(1)–Zn–O(11) 107.4(1), O(2)–Zn–O(11) 109.4(1).

of sodium-hopping in solution, being frozen out in the crystal or of the coexistence of several isomers of the molecule $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2(\text{Na})]_4 \cdot 5(\text{THF})$.

The inner skeleton of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ consists of two $\text{Al}_2\text{O}_3\text{Zn}$ six-membered rings in a typical boat conformation and which are related by a centre of symmetry (Fig. 3). The molecule $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ therefore is centro-symmetric. At the zinc corners of the boat, both six-membered rings are connected by a Zn–O-bond to an oxygen atom (O(1)) which is further linked to two aluminium atoms and which displays an almost planar metal environment (average sum of the angles: $356.1(1)^\circ$). The zinc atoms are in distorted tetrahedral oxygen coordination sites. This coordination site is built up by two hydroxide groups (O(2) and O(3)) and an oxygen atom (O(11)) of a diethylether. The average value of Zn–O bond lengths is 1.97(1) Å, with the Zn–O(11) bond with 1.998(3) Å being apparently longer than the other ones, diethyl ether behaving as a Lewis base. The mean bond distance around the aluminium atoms is 1.76(2) Å; two categories can be distinguished: those of oxygen atoms binding between aluminium or aluminium and zinc atoms (range: 1.783(2)–1.800(2) Å) and those connecting aluminium and silicon atoms (range: 1.699(2)–1.736(2) Å). These differences reflect the different capabilities of the electropositive elements to withdraw electron density.

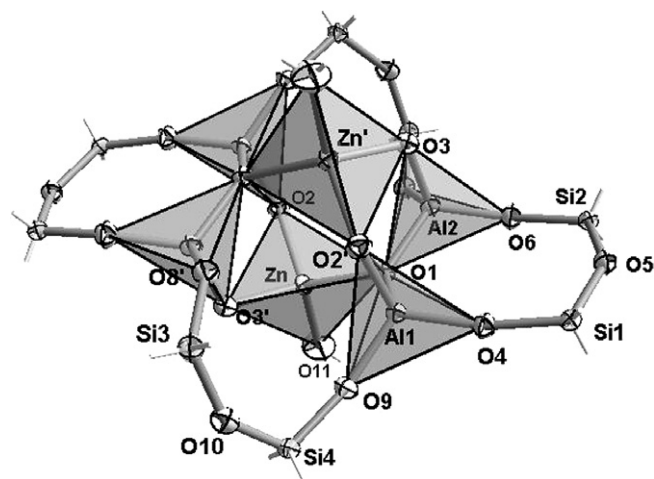


Fig. 4. Molecular structure of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{O}-\text{H})]_2 \cdot 2(\text{OEt}_2)$ with oxygen polyhedra around the aluminium and zinc atoms; the anisotropic displacement ellipsoids are drawn with 50% probability. (The carbon atoms have been omitted for clarity.)

The former $\text{Al}_4(\text{O}[\text{H}])_4$ eight-membered core of $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_4$ has been changed in $[\text{Ph}_2\text{SiO}]_8[\text{AlO}(\text{OH})]_2[\text{AlO}_2]_2[\text{Zn}(\text{OH})]_2 \cdot 2(\text{OEt}_2)$ due to the incorporation of the zinc atoms while the four outer loops $-\text{O}-[\text{Ph}]_2\text{Si}-\text{O}-[\text{Ph}]_2\text{Si}-\text{O}-$ remain almost unchanged (even with respect to geometrical orientation). This can be better illustrated by a polyhedron representation of the metal oxide core (with the oxygen atoms forming the edges of the tetrahedra) (Fig. 4). It also becomes clear from this picture that all zinc and aluminium centred tetrahedra are connected by edge sharing with the O(1) being the only edge sharing three polyhedra. Another interesting point is the formal cleavage of two former Al–O[H]–Al connections (see O(2) and O(3)).

3. Experimental

3.1. General

All synthetic procedures have been performed under nitrogen with strong exclusion of air and moisture in Stock-type apparatus. The IR-spectra were obtained using a BIO-RAD FT 165 spectrometer, NMR-spectra using a BRUKER AC 200 F (^1H , ^{13}C) or AC 200 P (^{29}Si). CHN analytical data were derived from an “elemental analyser” of the LECO corporation.

3.2. Crystal structure determinations

The data collection was performed on a Stoe imaging plate (IPDS I) diffractometer. The structures were solved by direct methods and refined by full-matrix least squares cycles with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms are fixed and refined as rigid groups. All calculations were done using the SHELX [22] program system.

3.3. $[(C_6H_5)_2SiO]_8[AlO_2(Na)]_4 \cdot 5(THF)$

1.94 ml (3.88 mmol) (2 M THF solution) sodiumcyclopentadienyl was slowly added to 2.06 g (0.97 mmol) alumopolysiloxane $[Ph_2SiO]_8[AlO(OH)]_4 \cdot 4OEt_2$ in 15 ml THF. The dark violet solution of the sodiumcyclopentadienyl was decoloured by slowly adding it to the alumopolysiloxane. The reaction solution mists through precipitation of a white solid material. After about 6 h, the solid material was filtered from the mother solution, and colourless crystals of $[(C_6H_5)_2SiO]_8[AlO_2(Na)]_4 \cdot 5(THF)$ with a yield of 1.43 g (66.82%) were obtained. $C_{116}H_{120}Si_8O_{21}Al_4Na_4$ (2274.7 g/mol): C 62.16 (calc. 61.25), H 5.13 (calc. 5.32). 1H NMR (THF/ C_6D_6): $\delta = 1.8$ (s, THF), 3.7 (s, THF) 6.42–6.51 (m, C_6H_5), 6.86–6.91 (m, C_6H_5) ppm. ^{13}C NMR (THF/ C_6D_6): $\delta = 26.37$ ($(CH_3CH_2)_2$), 68.27 ($(CH_3CH_2)_2O$), 128.1 (C_6H_5), 129.8 (C_6H_5), 135.3 (C_6H_5), 140.7 (C_6H_5) ppm. ^{29}Si NMR (THF/DMSO- d_6): $\delta = -39.18$ ppm. ^{29}Si -MAS NMR: -45.35 (s), -47.56 (s), -48.54 (s), -49.16 (s) ppm.

3.4. $[(C_6H_5)_2SiO]_8[AlO(OH)]_2[AlO_2]_2[Zn(OH)]_2 \cdot 2(OEt_2)$

0.74 ml (1.74 mmol) of a 2 M dimethyl-zinc toluene solution, diluted in further 3 ml toluene, was slowly added to 1.56 g (0.74 mmol) of the alumopolysiloxane $[Ph_2SiO]_8[AlO(OH)]_4 \cdot 4OEt_2$ in 7 ml anhydrous toluene. On stirring, a strong evolution of methane can be observed. After a few hours, the reaction solution turns into a cloudy white colour. The reaction mixture was stirred at room temperature overnight. The formed precipitation was separated from the mother solution by filtration. The precipitation is only soluble in THF. Colourless crystals were obtained in a yield of 1.43 g (91.67%) from the reaction solution. $C_{118}H_{118}Si_8O_{20}Al_4Zn_2$ (2319.5 g/mol): C 61.25 (calc. 61.10), H 5.04 (calc. 5.13). 1H NMR (THF/ C_6D_6): $\delta = 6.85$ –7.21 (m, C_6H_5), 7.41–7.80 (m, C_6H_5) ppm. ^{13}C NMR (THF/ C_6D_6): $\delta = 15.02$ ($(CH_3CH_2)_2$), 65.00 ($(CH_3CH_2)_2O$), 128.4 (C_6H_5), 129.2 (C_6H_5), 134.9 (C_6H_5), 135.2 (C_6H_5), 137.9 (C_6H_5) ppm. ^{29}Si NMR (dioxane/ C_6D_6): $\delta = -43.66$, -44.68, -45.59 ppm. IR (3800–

3200 cm^{-1}): 3380 cm^{-1} . Calculations are based on two toluene molecules/formula unit.

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