Letter

A convenient route to anionic and cyclic aluminosiloxanes: crystal structures of $[PyH][\overline{Al\{OSiPh_2(OSiPh_2)_2O}\}_2]$ and the first twelve-membered organic aluminosilicate $Al_2Si_4O_6$ ring

Yurii K. Gun'ko,[*a] **Roisin Reilly**[a] **and Vadim G. Kessler**[b]

[a] *The Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland*
[b] *Department of Chemistry, Swedish University of Agricultural Sciences Box 7015, 75007 Uppsala, Sweden*

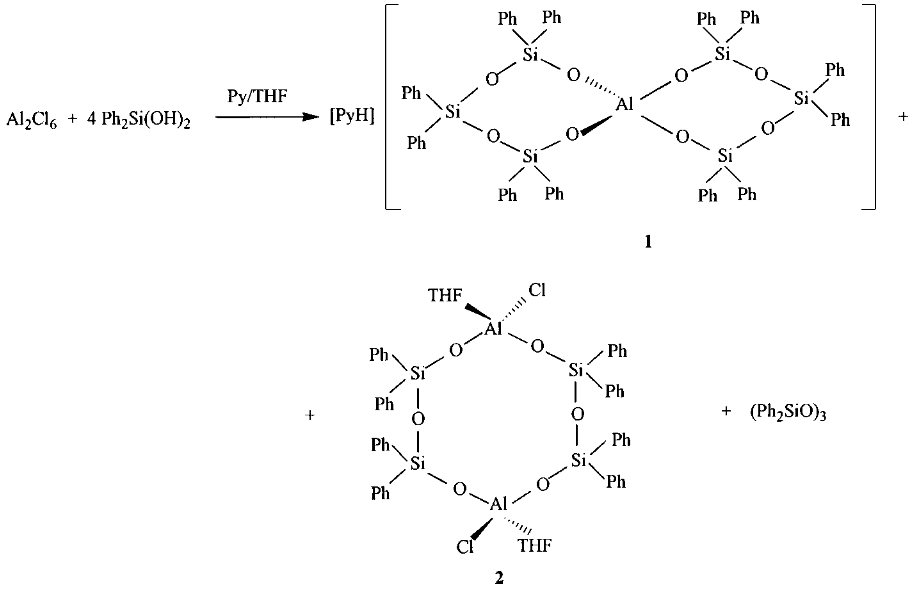
Received (in Cambridge, UK) 27th November 2000, Accepted 31st January 2001
First published as an Advance Article on the web 15th March 2001

The reaction of Al_2Cl_6 with an excess of $Ph_2Si(OH)_2$ in THF in the presence of pyridine yielded new anionic and cyclic aluminosiloxanes: the structure of the anionic complex is composed of separated pyridinium cations and aluminosiloxane anions with a tetrahedral arrangement around the Al atom, which is similar to that in natural aluminosilicates; the core of the cyclic aluminosiloxane is a twelve-membered $Al_2Si_4O_6$ ring in a chair conformation, which contains a Cl group on each of the two Al atoms.

Controlled-pore inorganic and organic solids play a key role in modern chemical technology as heterogeneous catalysts, adsorbents, porous membranes, host matrices for pharmacology, electronics and nanotechnology. Zeolites are one of the best known and important examples of metal-containing porous materials.[1] Metallasiloxanes containing Si–O–M functional groups (M = main group or d-transition metal) have been envisaged as relevant molecular models for mimicking the surface sites of zeolite-type catalysts.[2] Several soluble aluminosiloxanes containing four-[3] six- and eight-membered[4,5] rings and also aluminosilasesquioxanes[6] have been reported previously. Here, we report a straightforward synthetic route for the preparation of a new anionic aluminosiloxane and the first twelve-membered aluminosiloxane ring, and their structural characterization.

The reaction of aluminium chloride with four equivalents of $Ph_2Si(OH)_2$ in THF in the presence of an excess of pyridine proceeds with the precipitation of PyHCl, identified by NMR and elemental analysis, affording two new aluminosiloxanes; anionic $[PyH][\overline{Al\{OSiPh_2(OSiPh_2)_2O}\}_2]$ (**1**) and cyclic $[\{(Ph_2SiO)_2O\}AlCl(THF)]_2$ (**2**) in 53 and 16% yields, respectively (Scheme 1).† The products were isolated by fractional crystallisation from THF. Further examination of the remaining mother liquor by NMR spectroscopy also revealed the presence of a fully condensed trisiloxane, $(Ph_2SiO)_3$. The formation of at least three different products indicates a fairly sophisticated mechanism for the process. The reaction presumably involves the Lewis acid (Al_2Cl_6) catalysed condensation of $Ph_2Si(OH)_2$ to higher siloxanes containing $–OSiPh_2OPh_2SiO–$ and $–OSiPh_2(OSiPh_2)Ph_2SiO–$ units, followed by pyridine-assisted metathesis between the ligands and Al_2Cl_6.

Both compounds **1** and **2** provide satisfactory elemental analysis. The IR spectrum of **1** in Nujol contains characteristic Si–O–Si stretching bands between 1012–1120 cm^{-1} and pyridinium absorbances at 3162, 1589, 721 and 700 cm^{-1}.† The ^1H NMR spectrum of **1** in C_6D_6 shows a complex spectrum with a number of multiplets relating to pyridinium cations and to the $Ph_2Si–$ fragments. The resonances due to *o*-protons of the $SiPh_2–$ groups are shifted substantially downfield (7.83–7.99 ppm) compared to those of the *m*- and *p*-protons of Ph-groups (7.01–7.09 ppm) that have been observed before for



Scheme 1

528 *New J. Chem.*, 2001, **25**, 528–530 DOI: 10.1039/b009556g

aluminium complexes with the Ph_3SiO– and $O(Ph_2SiO–)_2$ ligands.[5] In the $^{13}C\{^1H\}$ NMR spectrum of **1**, three carbon resonances due to the pyridinium and a number of resonances arising from aromatic carbons were observed. $^{29}Si\{^1H\}$ NMR of **1** reveals two signals for two different types of $SiPh_2$ fragments at −42.36 and −43.56 ppm in a 1 : 2 ratio. The resonance related to α-silicones, which are close to the Al centre, occurs at slightly higher field.

X-Ray quality crystals of **1** were obtained from a concentrated solution in THF at 0 °C. The structure consists of well-separated pyridinium cations and aluminoxane anions (Fig. 1).‡ The closest N (cation)···C(anion) contact is 4.276 Å. In the anion, the Al atom is coordinated by four oxygen atoms of two cyclic siloxane fragments having a slightly distorted tetrahedral arrangement (Fig. 1) with O–Al–O angles varying from 106.45(13) to 111.30(13)°. A similar coordination mode for the same ligand was initially reported for Ti in *cis*-$[\overline{Ti\{OSiPh_2(OSiPh_2)_2O}\}_2(py)_2]_2 \cdot C_6H_5Me$, but in the latter the Ti is additionally coordinated by two pyridine molecules providing distorted octahedral geometry.[7] Preliminary reported structures of $(PhBO)(Ph_2SiO)_3$,[8] $[(py)_2Li]_2$-μ-$Mg[\{Ph_2SiO\}_2O][\{Ph_2SiO_3\}_3O]$[9] and the monometallated derivative $[K\{O(Ph_2SiO)_2SiPh_2OH\}]_2 \cdot C_6H_6$[10] also contain the same ligand, but in different coordination modes. Two puckered eight-membered aluminosiloxane rings in **1** lie in perpendicular planes, similarly to those in *cis*-$[\overline{Ti\{OSiPh_2(OSiPh_2)_2O}\}_2(py)_2]_2 \cdot C_6H_5Me$.[7] The eight-membered aluminosiloxane rings may also be considered as four-membered, counting only tetrahedral atoms (Al and Si), such as referred to in zeolites. The diameter of the aluminosilicate rings in **1** is about 4.2–4.3 Å, *i.e.* comparable to those in zeolites such as, for example, NaY.[11] Al–O bond lengths in **1**, ranging from 1.723(3) to 1.772(3) Å, with an average of 1.738 Å, are longer than the corresponding ones in non-anionic aluminosiloxanes {*e.g.* from 1.714(4) to 1.718(4) Å in $[(c\text{-}C_6H_{11})_7Si_7O_{12}Al(OPPh_3)]$[6b]}, but are comparable to those in other anionic aluminosiloxane structures, *e.g.* $[\{Na(thf)_4\}][\{EtAlO_3SiR\}_4]$ [1.753(4)–1.784(4) Å],[4b] $[HNEt_3]_2[\{(Ph_2Si)_2O_3\}_4Al_4O_2(OH)_2]$ [1.715(3)–1.829(4) Å],[5b] and $[HNEt_3][\{(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)O_2\}_2Al] \cdot C_6H_{14}$ [1.725(7)–1.788(6) Å].[6c] Si–O bond lengths in **1** range from 1.588(3) to 1.647(3) Å, with an average of 1.619 Å. The average Si–O and Al–O bond lengths in **1** are comparable to the idealised Si–O (1.603 Å) and Al–O (1.761 Å) distances in natural tetrahedral aluminosilicates.[12]

The IR spectrum of **2** in Nujol contains a very broad band, characteristic of Si–O–Si stretching, with the maximum at 1091 cm^{-1}.† ^1H NMR of **2** reveals multiplets at 7.02–7.07 ppm for the *m*- and *p*-protons, and at 7.89 ppm for the *o*-protons of the Ph_2Si– groups; signals of THF are also observed. The $^{13}C\{^1H\}$ NMR spectrum of **2** reveals several carbon resonances attributed to the aromatic carbons and characteristic THF peaks. The $^{29}Si\{^1H\}$ NMR spectrum of **2** contains only one signal from $SiPh_2$ at −44.77 ppm.

X-Ray quality crystals of complex **2** were crystallised from a concentrated THF solution at −22 °C. The major difficulty in the investigation of the crystal structure of **2** by the X-ray single crystal method was rather poor reflection of the X-rays.‡ Even for quite large (about 1 mm) and well-shaped single crystals, no reflections with sufficient intensity $[I > 2\sigma(I)]$ could be observed at θ greater than 15°. We therefore decided to apply 0–15° limits for θ for the data used in the structure refinement. The low reflection capacity at high angles appears to be a more-or-less general feature for metallasilsesquioxane derivatives, indicating irregularities in the long-distance ordering.[5b] An extra cause of long-range disorder in the present compound may in fact be due to incomplete population of the sites occupied by guest THF molecules in its crystal structure. However, the problems above do not significantly affect the aluminosiloxane core of the molecule and the standard deviation in bond lengths and angles in the $Al_2Si_4O_6$ ring fall into the range usually observed and may be discussed here. The central fragment of **2**, a twelve-membered $Al_2Si_4O_6$ ring (Fig. 2), occurs in natural aluminosilicates.[11] However, to the best of our knowledge, aluminosiloxane analogues have not yet been isolated. Again, counting only tetrahedral atoms (Al and Si) as was used to be common in zeolite chemistry, the twelve-membered aluminosiloxane ring can be considered as six-membered. The $Al_2Si_4O_6$ ring has a chair conformation with Si2 and Si2′ atoms lying at 1.332(3) Å above and below the plane formed by the other ten atoms. A chair conformation was also reported for the eight-membered $Al_2Si_2O_4$ ring in $[RN(SiMe_3)Si(OH)O(OAlBu^i \cdot THF)]_2$ ($R = 2,6\text{-}Pr^i_2C_6H_3$), having two oxygen atoms out of the plane.[4a] Each Al atom in **2** is coordinated by three oxygen atoms (two from siloxane and one from THF) and one chlorine atom and has a distorted tetrahedral arrangement with angles around Al of 103.4(8) to 118.5(8)°. In the ring, the Al–O bond lengths of 1.645(17) and 1.662(17) Å (average of 1.654 Å) are shorter than those in **1** and in any other reported aluminosiloxanes: the closest average endocyclic Al–O bond length of 1.71 Å is in $[RN(SiMe_3)SiO_3Al \cdot dioxane)]_4$ ($R = 2,6\text{-}Pr^i_2C_6H_3$).[4b] As expected, the Al–O bond to the THF molecule [1.870(16) Å] is longer and close to that of 1.879(5) Å in

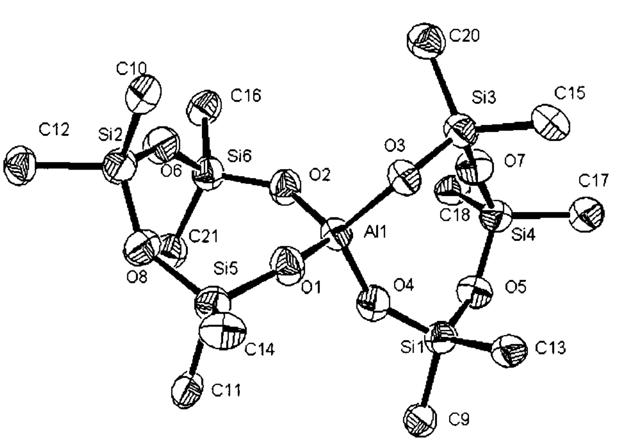


Fig. 1 Crystal structure of the $[\overline{Al\{OSiPh_2(OSiPh_2)_2O}\}_2]^-$ anion in **1** (only the *ipso* carbon atoms of the aromatic rings are shown for clarity). Selected bond lengths (Å) and angles (°): Al1–O1 1.733(3), Al1–O2 1.723(3), Al1–O3 1.772(3), Al1–O4, 1.724(3); O1–Al1–O3 106.45(13), O2–Al1–O4 111.26(14), O2–Al1–O1 111.30(13), O4–Al1–O1 109.88(14), O2–Al1–O3 108.59(13), O4–Al1–O3 109.22(13).

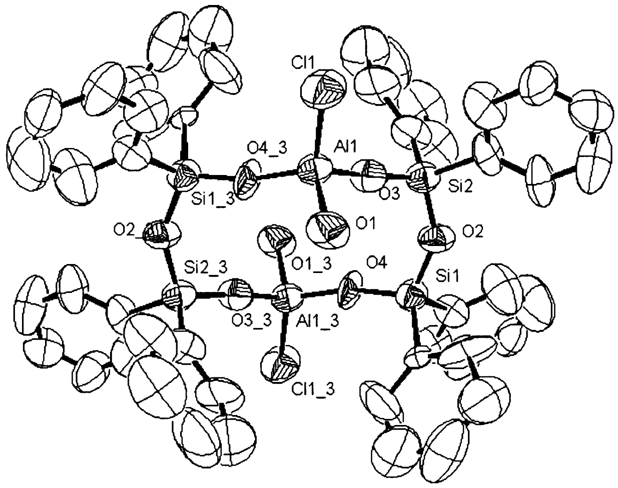


Fig. 2 Crystal structure of $[\{(Ph_2SiO)_2O\}AlCl(THF)]_2$ (**2**) (only the oxygen atoms of the THF molecules are shown for clarity). Selected bond lengths (Å) and angles (°): Al1–O1 1.870(16), Al1–O3 1.645(17), Al1–O4 1.662(17), Al1–Cl1, 2.111(8); O1–Al1–O3 104.0(8), O3–Al1–O4 118.5(8), O4′–Al1–O1 105.80(10), O3–Al1–Cl1 111.3(6), O4′–Al1–Cl1 112.2(6), O1–Al1–Cl1 103.4(8).

$[RN(SiMe_3)Si(OH)O(OAlBu^i \cdot THF)]_2$ (R = 2,6-$Pr^i_2C_6H_3$).[4a] The Al–Cl bond length of 2.111(8) Å is comparable to those reported in the four-membered $[Me_2HSiOAlCl_2]_2$ [2.080(1) and 2.084(1) Å].[3] The silicon atoms also have a distorted tetrahedral geometry, with bond angles of 103.9(14) to 113.9(13)°. The Si–O bond lengths vary from 1.579(16) to 1.638(17) Å, with an average of 1.607 Å, which is comparable to those in **1** and other aluminosiloxanes, and extremely close to the idealised Si–O distance (1.603 Å) in natural tetrahedral aluminosilicates.[12] Compound **2** is interesting for several reasons. Since the two Al centres are available for coordination to Lewis bases like ethers or amines, **2** might be used for the corresponding host–guest reactions. The structure of **2** does incorporate THF guest molecules, which are located in the packing cavities of the $Al_2Si_4O_6$ rings, in addition to THF molecules coordinated by the Al atoms. Another remarkable feature of **2** is the presence of good leaving groups on each of the two Al atoms. These ligands can be easily replaced by other fragments or can be used for the bridging of aluminosiloxane rings into oligomeric or polymeric structures. This might be achieved *via* reaction of **2** with appropriate alkali metal derivatives or by amine-assisted metathesis with silanols. Thus, the aluminosiloxane **2** seems to be a promising starting material for the preparation of novel materials with controlled pore sizes.

In summary, both aluminosiloxanes **1** and **2**, appear to be interesting molecular models for some fragments in aluminosilicate minerals. We also suggest that these complexes might be used as precursors for the preparation of other aluminosiloxanes and polyaluminosiloxanes.

Acknowledgement

We are grateful to Enterprise, Ireland, and Trinity College, Dublin, for providing a studentship to R. R. and for other support.

Notes and references

† *Representative synthesis and selected spectroscopic data* for **1** and **2**: Dry pyridine (4.4 ml, 58.5 mmol) was added *via* syringe to the mixture of aluminium chloride (0.78 g, 2.92 mmol) and diphenylsilanediol (2.33 g, 10.75 mmol) in THF (150 cm^3). The mixture was stirred for 24 h, then filtered and the filtrate removed *in vacuo*. The residue was washed with hexane and dried *in vacuo*. Fractional re-crystallisation from concentrated THF solution at ambient temperature afforded colourless crystals of **1** (1.26 g, 53%). Found: C, 70.1; H, 5.02; $C_{77}H_{66}AlNO_8Si_6$ requires: C, 69.5; H, 4.97%. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.99–7.83 (m, 16H, C_6H_5, *o*), 7.34 (s, 1H, PyH), 7.23 (br, 2H, PyH), 7.09–7.01 (m, 24H, C_6H_5, *m*, *p*), 6.42 (m, 1H, PyH), 5.92 (m, 2H, PyH). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 22 °C): δ 146.94 (Py), 138.85 (Ph), 137.50 (Ph), 135.03 (Ph), 134.83 (Ph), 129.75 (Ph), 129.03 (Ph), 128.03–127.25 (Ph), 124.33 (Py), 114.29 (Py). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 22 °C): δ −42.36 (s, 1, β-Si), −43.56 (s, 2, α-Si). IR (Nujol, cm^{-1}): 3162 (br), 2725 (s), 2670 (m), 1732 (s), 1589 (m), 1288 (m), 1120 (s), 1055 (m), 1012 (m), 991 (s), 939 (m), 721 (s), 700 (s), 627 (m), 588 (m).

Further concentration of the mother liquor and cooling to −22 °C gave colourless crystals of **2** (0.49 g, 16%). Found: C, 63.8; H, 5.82; $C_{60}H_{64}Al_2Cl_2O_7Si_6$ requires: C, 63.5; H, 5.64%. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.89 (m, 16H, C_6H_5, *o*), 7.02–7.07 (m, 24H, C_6H_5, *m*, *p*), 3.49 (m, 8H, THF), 1.35 (m, 8H, THF). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 22 °C): δ 134.71 (Ph), 134.46 (Ph), 130.68 (Ph), 128.10–127.80 (Ph), 68.10 (THF), 26.09 (THF). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 22 °C): δ −44.77 (Ph_2Si). IR (Nujol, cm^{-1}): 2720 (m), 1963 (s), 1894 (s), 1826 (s), 1778 (s), 1665 (s), 1606 (s), 1591 (s), 1537 (m), 1259 (m), 1091 (br,m), 969 (m), 804 (m), 720 (s), 694 (m).

‡ *Crystal data* for **1**: $C_{77}H_{66}AlNO_8Si_6$, $M = 1328.83$, triclinic, space group $P\bar{1}$, $a = 11.8800(9)$, $b = 15.0636(12)$, $c = 20.7172(17)$ Å, $\alpha = 93.716(2)$, $\beta = 102.95(3)$, $\gamma = 107.226(2)°$, $U = 3519.1(5)$ Å^3, $T = 295(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.187 mm^{-1}, 14 160 reflections collected, 9181 independent reflections [R(int) = 0.0325], $R_1 = 0.0540$ for reflections with $I > 2\sigma(I)$, $wR_2 = 0.1284$ (all data).

For **2**: $C_{60}H_{64}Al_2Cl_2O_7Si_6$, $M = 1134.33$, monoclinic, space group $P2_1/n$, $a = 14.275(4)$, $b = 16.322(4)$, $c = 16.560(4)$ Å, $\beta = 113.911(6)$, $U = 3527.3(16)$ Å^3, $T = 295(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.227 mm^{-1}, 5251 reflections collected, 1420 independent reflections [R(int) = 0.1731], $R_1 = 0.0780$ for reflections with $I > 2\sigma(I)$, $wR_2 = 0.2025$ (all data).

Data for both structures were collected on a Bruker SMART CCD 1K diffractometer. Structures were solved by direct methods (SHELXTL-NT) and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the final solution for **1** using a riding model and refined in isotropic approximation. No attempts have been made to locate the hydrogen atoms in the structure of **2**.

CCDC reference numbers 153283 and 153284. See http://www.rsc.org/suppdata/nj/b0/b009556g/ for crystallographic files in CIF or other electronic format.

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