DALTON
COMMUNICATION

Synthesis and crystal structure of [K{O($Ph_2SiO)_2SiPh_2OH$}]$_2$·C_6H_6; the first structurally characterised example of a monometallated derivative of an α,ω-siloxane diol. Solution chemistry in relation to KOH-promoted ring-opening polymerisation of $(Ph_2SiO)_3$

Barbara Laermann, Michael Lazell, Majid Motevalli and Alice C. Sullivan*

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

The first structurally characterised example of a monometallated derivative of an α,ω-siloxane diol compound [K{O($Ph_2SiO)_2SiPh_2OH$}]$_2$·C_6H_6 has been isolated {from [($Ph_2SiOH)_2O$] and KOBu^t, 1 : 1 molar ratio} and structurally characterised by X-ray crystallography, proton NMR, IR and variable-temperature ^{29}Si NMR and its chemistry in relation to KOH-promoted ring-opening polymerisation of $(Ph_2SiO)_3$ is discussed.

The co-ordination chemistry of α,ω-siloxane diolates [($R_2SiO)_n$-O]$^{2-}$ represents one area of metallasiloxane chemistry[1] which also covers metal complexation by a range of other important siloxanolate ligand types, for example, species with $RSiO_3$, R_2SiO_2 and R_3SiO functionalities. Some of these compounds are of interest both as precatalysts for olefin polymerisation and as precursors for metal oxide–silica materials.[1] In recent years we have described a number of co-ordination compounds derived from the dilithium and disodium salts of the disiloxane diol [($Ph_2SiOH)_2O$].[2] The direct reaction between metal and diol was employed for the formation of the disodium compound but we were unable to isolate a potassium compound in this way. Thus we investigated alternative routes to such reagents. In the course of this we investigated the reaction between [($Ph_2SiOH)_2O$] and KOBu^t in toluene–tetrahydrofuran (thf), molar ratio 1 : 1, and isolated the compound [K{O($Ph_2SiO)_2SiPh_2OH$}]$_2$·C_6H_6 **1** in 12% yield after two recrystallisations of the first crop from hot toluene–benzene.† We have previously observed chain expansion from disiloxane in [($(Ph_2SiO)_2O$]$^{2-}$ to trisiloxanediolate [O($Ph_2SiO)_2SiPh_2O$]$^{2-}$ during the transfer of the diolate ligand from the dilithium and disodium salts to Sn^{IV} and some transition metals.[2] The formation of the dilithium and disodium reagents themselves however proceeded without such chain expansion.[3] The formation of **1** as described here proceeds with chain expansion. Compound **1** is sparingly soluble in aromatic hydrocarbons but dissolves readily in chloroform, thf, ethanol and acetone. A powdered sample of **1** appeared unchanged (by IR) after standing in air for 30 min. While some monometallated derivatives of diorganosilanediols have been characterised, *e.g.* [Li{OSi(OH)Bu$^t_2$}]$_4$ [4] and [Na{OSi(OH)Bu$^t_2$}·thf]$_6$,[5] compound **1** is the first example of a structurally characterised monometallated α,ω-siloxane diol.

One of the standard routes to silicone polymers involves KOH in anionic ring-opening polymerisation of cyclic siloxanes[6] and it is generally accepted that catalytic activity depends on the presence of free ion pairs which are in equilibrium with dormant associated ion pairs.[6,7] Much of the evidence is derived from extensive analysis of the kinetics as well as solution conductivity during polymerisation. It is possible that structure **1** might represent the associated product of the first step in the ring-opening polymerisation of $(Ph_2SiO)_3$. We investigated the reaction between KOH and $(Ph_2SiO)_3$ (1 : 1) in dry 5% toluene in ethanol, at room temperature. A crop of colourless crystals deposited from a solution of the reaction products in toluene at −25 °C was not compound **1** but $(Ph_2SiO)_4$. Ring-opening polymerisations of cyclic siloxanes are known to proceed initially to the linear polymer with subsequent rearrangement to the more thermodynamically stable cyclics.[6] However compound **1** itself showed no activity towards $(Ph_2SiO)_3$ in refluxing thf [**1** : $(Ph_2SiO)_3$, 1 : 0.01]. The cyclic trimer $(Ph_2SiO)_3$ was recovered unchanged, and this suggests that **1** remains associated in thf solution and is not in equilibrium with an ion pair which might have promoted ring-opening oligomerisation. However compound **1**, not surprisingly, does react with KOH (molar ratio 10 : 1) in toluene–ethanol as evidenced by changes in the IR spectrum of the product (products not characterised). Thus, the isolation of $(Ph_2SiO)_4$, rather than compound **1**, from the reaction between KOH and $(Ph_2SiO)_3$ suggests either that compound **1** once formed competes with $(Ph_2SiO)_3$ for reaction with KOH and these initial products react with $(Ph_2SiO)_3$, or that a reactive monomeric version of **1** is formed which can promote oligomerisation of $(Ph_2SiO)_3$ before the dimer **1** can form.

The crystal structure of **1**‡ shows two independent molecules

---

† Compound **1**. To a suspension of KOBu^t (0.90 g, 8.10 mmol) in toluene (50 cm^3) at 0 °C was added a solution of [($Ph_2SiOH)_2O$] (3.34 g, 8.10 mmol) in thf (15 cm^3). This mixture was stirred for 3 h, the solvent evaporated and the residue extracted with toluene (*ca.* 30 cm^3). The toluene extract was concentrated until turbid. A clear solution was obtained on heating and colourless crystals of **1** were obtained on slow cooling to room temperature. These were recrystallised from toluene–benzene (9 : 1) to give 0.7 g of **1** (12% based on available potassium). Material remaining in the mother-liquors was not further characterised. For compound **1** m.p. 120–122 °C (Found: C, 68.05; H, 5.15. Calc. for $C_{78}H_{68}K_2O_8Si_6$: C, 67.9; H, 4.95%). ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.7 (m, *m*-H of Ph) and 7.2 (m, *o*- and *p*-H of Ph). ^{29}Si NMR (acetone/[$^2H_6$]acetone, 193 K): δ −42.1 (s) and −46.6 (s), relative intensity 2 : 1. IR (Nujol, cm^{-1}): 3500w (br), 1588m, 1429s, 1261m, 1119s, 1038s, 997s, 938s, 802m, 755m, 743m, 700s, 627w, 614w, 526s and 508s.

‡ Crystal_data for $C_{78}H_{68}K_2O_8Si_6$: cube, $M = 1378.28$, triclinic, space group $P1$, dimensions 0.34 × 0.45 × 0.24 mm, $a = 12.119(1)$, $b = 13.219(1)$, $c = 24.460(2)$ Å, $\alpha = 103.44(2)$, $\beta = 77.13(1)$, $\gamma = 100.98(2)°$, $U = 3675.5(5)$ Å^3, $Z = 2$, $D_c = 1.245$ Mg m^{-3}, $F(000) = 1440$, μ(Mo-Kα) = 0.281 mm^{-1}. Data were collected at ≈293 K on a CAD4 diffractometer using Mo-Kα radiation (λ = 0.710 69 Å) and were not corrected for absorption. The structure was solved by standard heavy atom techniques (SHELXS 86)[8] and refined by full-matrix least-squares (on F^2) (SHELXL 93)[9] with phenyl groups treated as rigid hexagons [C−C 1.395 Å, C−C−C 120°, and with inclusion of hydrogen atoms at fixed positions C−H 0.93 Å]. A total of 10 202 reflections were measured of which 10 199 were used in the final refinement. Final $R1 = 0.0697$, $wR2 = 0.1636$ [$I > 2\sigma(I)$] and $R1 = 0.1763$, $wR2 = 0.1843$ (all data) for 705 parameters. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.00P]$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/456.

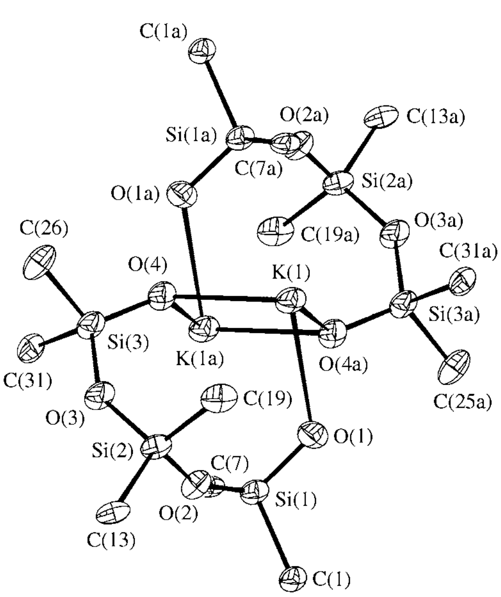
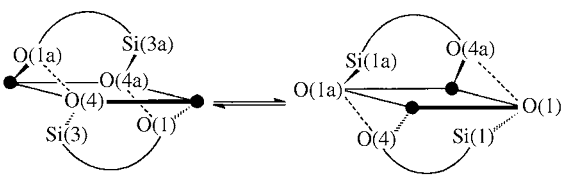


Fig. 1 Molecular structure of compound **1** (thermal ellipsoids at 50% probability level) along with selected bond lengths (Å) and angles (°): K(1)–O(1) 2.912(4), K(1)–O(4) 2.681(4), K(1)–O(4a) 2.812(4), Si(1)–O(1) 1.604(4), Si(1)–O(2) 1.638(4), Si(2)–O(2) 1.600(4), Si(2)–O(3) 1.607(4), Si(3)–O(4) 1.584(4), Si(3)–O(3) 1.646(4); O(4)–K(1)–O(4a) 87.46(13), O(4)–K(1)–O(1) 91.42(13), O(4a)–K(1)–O(1) 50.98(12), K(1)–O(4)–K(1a) 92.54(13), Si(1)–O(4)–K(1) 123.7(2), Si(3)–O(4)–K(1) 134.4(2), Si(3)–O(4)–K(1a) 118.1(2), angles at Si are close to tetrahedral values

with slightly different conformations in the unit cell and one of these is shown in Fig. 1 along with selected bond lengths and angles. A dimeric centrosymmetric structure is found where the two halves of the dimer are linked through a four-membered planar, rectangular K_2O_2 ring. Pseudo-pyramidal geometry at each potassium is completed by co-ordination of the terminal hydroxyl group of the trisiloxanol residue in each half of the dimer. The tricyclic structure thus formed consists of two non-planar eight-membered potassiotrisiloxanol rings lying on opposite sides of the central K_2O_2 potassiooxane ring at angles defined by K(1a)–O(4)–Si(3) 118.1(2)° and O(4a)–K(1)–O(1) 50.98(12)°. The hydroxyl proton was not located but its position close to O(1) is inferred from a comparison of the co-ordination modes adopted by O(1) and O(4) as well as the K–O and Si–O distances associated with these oxygens where those to O(1) are considerably longer in both cases as expected. The extremely acute nature of the O(4a)–K(1)–O(1) angle however suggests the presence of a hydrogen bond between O(1) and O(4a) [O(1)···O(4a) 2.42 Å]. It is noteworthy that the related hexaphenyltrisiloxane-1,5-diol $[(HOPh_2SiO)_2SiPh_2]$ also adopts a dimeric structure where two eight-membered HSi_3O_4 rings are linked through an eight-membered O_4H_4 heterocycle.[10] The pyramidal geometry at potassium stemming from the oxygen ligation belies apparently close potassium phenyl ring contacts K(1a)–$[C(7)–C(12)]_{ave}$ 3.346 Å, K(1a)–C(19) 3.157(5) Å and K(1a)–C(20) 3.185(5) Å. These contacts are within the range of potassium–arene carbon distances reported in the literature for $[(C_6H_6)KOSiMe_2Ph]_4$[11] $K[MeSe(AlMe_3)]\cdot 2C_6H_6$[12] and $[\{(Me_3Si)_2HC\}_3Lu(\mu\text{-}Cl)K(C_6H_5Me)_2]$,[13] where K–$(C_6)_{ave}$ is 3.275, 3.31 and 3.51 Å respectively.



Scheme 1 Equilibration of Si(1)/Si(3) environments *via* hydroxyl proton exchange. Dashed lines indicate the position of hydrogen bonds

The appearance of only two signals, intensity ratio 2 : 1, in the solution phase ^{29}Si NMR spectrum (recorded in $CDCl_3$, thf and acetone) instead of the expected three on the basis of the solid-state structure, and the absence of any peaks that could be assigned to the hydroxyl proton in the ^1H NMR spectrum (the IR spectrum shows a weak broad peak at 3500 cm^{-1}) may be indicative of an equilibration process involving the hydroxyl proton. The ambient temperature ^{29}Si NMR spectrum from an acetone solution of **1** persisted at −80 °C suggesting rapid exchange even at this low temperature. Assuming the dimeric structure is retained in solution possible equilibration of the Si(1)/Si(3) environments *via* exchange of hydroxyl protons between O(1)/O(4a) and O(1a)/O(4) is illustrated in Scheme 1.

References

1 R. Murugavel, A. Voigt, M. G. Walawalker and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205.
2 M. Lazell, M. Motevalli, S. A. A. Shah, C. K. S. Simon and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1996, 1449.
3 M. Motevalli, D. Shah and A. C. Sullivan, *J. Organomet. Chem.*, 1996, **513**, 239.
4 U. Klingebiel and D. Schmidt-Base, *Chem. Ber.*, 1989, **122**, 815.
5 U. Klingebiel, S. Schutte and D. Schmidt-Base, *Z. Naturforsch., Teil B*, 1993, **48**, 263.
6 S. S. Brown, T. C. Kendrick, J. McVie and D. R. Thomas, *Silicones* in *Comprehensive Organometallic Chemistry II*, ed. A. G. Davies, Pergamon, Oxford, 1995, vol. 2.
7 M. G. Voronkov, V. P. Meleshkevich and Yu. A. Yuzhelevskii, *The Siloxane Bond*, Consultants Bureau, New York, 1978.
8 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
9 G. M. Sheldrick, SHELXL 93, Programme for the Refinement of Crystal Structures, University of Göttingen, 1993.
10 H. Behbehani, B. J. Brisdon, M. F. Mahon and K. C. Molloy, *J. Organomet. Chem.*, 1993, **463**, 41.
11 M. J. McGeary, K. Folting, W. E. Streib and K. G. Caulton, *Polyhedron*, 1991, **10**, 2699.
12 J. L. Atwood and S. K. Seale, *J. Organomet. Chem.*, 1978, **155**, 1; J. L. Atwood, K. D. Crissinger and R. D. Rogers, *J. Organomet. Chem.*, 1976, **114**, 107.
13 C. J. Schaverien and J. B. Ban Mechelen, *Organometallics*, 1991, **10**, 1704.

Received 24*th December* 1996; *Communication* 6/08625J