

**Synthesis and Structural Characterisation of the Trinuclear Barium Disiloxanes [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(tetraglyme)<sub>2</sub>] and [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(hmpa)<sub>5</sub>(H<sub>2</sub>O)], containing an Unusual Ba<sub>3</sub>O<sub>7</sub> Core [tetraglyme = Me(OCH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>OMe; hmpa = (Me<sub>2</sub>N)<sub>3</sub>P=O]**

Jawwad A. Darr, Simon R. Drake,\* David J. Williams\* and Alexandra M. Z. Slawin

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY

Barium granules react with diphenylsilanediol in a mixed ammonia-toluene solution at -40 °C to yield [Ba(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>0.33</sub>] **1**, addition of either tetraglyme or hexamethylphosphoramide (hmpa) produces [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(tetraglyme)<sub>2</sub>] **2** and [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(hmpa)<sub>5</sub>(H<sub>2</sub>O)] **3**, respectively; complexes **2** and **3** are the first X-ray structurally characterised barium disiloxanes and contain an unusual trinuclear array of Ba cations incorporating an identical Ba<sub>3</sub>O<sub>7</sub> core.

The synthesis and study of metallocsiloxane polymers is of considerable interest to chemists, physicists and material scientists alike. This may be attributed to some of their unique properties, which include high thermal stability and electrical conductivity. Metal siloxanes of Sn, Pb, Mg, Cu and Hg were studied in the belief that modification of the related silicone structure may yield more thermally stable complexes.<sup>1</sup> Other early researchers in this area also investigated the reaction of alkaline media on a wide range of silanol ligands.<sup>2</sup> A notable study by Zietler and Brown,<sup>3</sup> on the reaction of Ph<sub>2</sub>Si(OH)<sub>2</sub> with Ti(Bu<sup>n</sup>)<sub>4</sub> yielded a spiro-siloxane complex, [Ti(OSiPh<sub>2</sub>OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>2</sub>]. While others have recently reported the spiro complex *cis*-(py)<sub>2</sub>[Ti(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>2</sub>] (py = pyridine).<sup>4</sup> These reactions demonstrate the facile coupling of silane diols to yield oligomeric siloxane rings, a feature which has been extensively studied by Sullivan and coworkers.<sup>4,5</sup> A recent example of another spiro-siloxane is the mixed transition metal-alkali metal complex, [Cu(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>2</sub>]-μ[Li(py)<sub>2</sub>] and also an unusual dilithium disiloxane compound [((py)LiO)<sub>2</sub>-OSi<sub>2</sub>Ph<sub>4</sub>]<sub>2</sub>.<sup>5</sup> A unifying feature, tying these diverse complexes together is the disiloxane ligand (OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sup>2-</sup>, which acts as an effective chelating or bridging ligand.<sup>4,5</sup>

Previous workers have explored the chemistry of triphenylsilanol with barium granules in ammoniacal-tetrahydrofuran (thf) and obtained the trinuclear barium complex [Ba<sub>3</sub>(O-SiPh<sub>3</sub>)<sub>6</sub>(thf)].<sup>6</sup> In an effort to widen our studies on M<sub>x</sub>{Si(OR)<sub>y</sub>}<sub>z</sub> based complexes, we now report the synthesis and characterisation of the first group 2 metal disiloxanes, based on the precursor complex [Ba(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>0.33</sub>] **1**, see Scheme 1. This complex was prepared from the treatment of barium granules with 2 equiv. of diphenylsilanediol in a saturated ammoniacal-toluene solution at -40 °C in *ca.* 97% yield.<sup>†</sup> This compound reacts readily with tetraglyme to yield [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(tetraglyme)<sub>2</sub>] **2** and with 2 equiv. of hmpa to produce [Ba<sub>3</sub>(OSiPh<sub>2</sub>OSiPh<sub>2</sub>O)<sub>3</sub>(hmpa)<sub>5</sub>(H<sub>2</sub>O)] **3**.

The IR spectra of complexes **1** and **3** both contain a broad band at 3200 cm<sup>-1</sup> which is assigned to an OH stretch of coordinated water, while for **1** an additional sharp band at

3380 cm<sup>-1</sup> is attributed to the NH<sub>3</sub> group.<sup>‡</sup> All of the complexes however show bands in the region 1120–1010 cm<sup>-1</sup> which previous workers have tentatively assigned as bands due to Si–O–Si stretching.<sup>4</sup>

Multinuclear (<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si) NMR spectroscopy of complexes **1–3** in either [<sup>2</sup>H<sub>6</sub>]benzene or [<sup>2</sup>H<sub>6</sub>]dimethyl sulfoxide reveals only time averaged disiloxane ligand signals.<sup>‡</sup> The <sup>29</sup>Si NMR spectroscopy of compounds **1–3** at room temp. is also surprisingly of little spectroscopic utility, with only single resonances observed. Evidently multinuclear NMR spectroscopy is not discriminating enough at room temp. to resolve the complex ligand rearrangements and site exchange processes which are most likely to be occurring.

Single crystals of **2**§ were obtained from a slowly cooled solution of hot toluene and for **3** from a toluene solution layered with n-hexane. The molecular structure of **2** is illustrated in Fig. 1. The structure has a central core containing three barium atoms, each bridged by the oxygen atoms of six diphenylsiloxide groups (Fig. 2). The central barium atom is seven coordinate, adopting a distorted edge bridged [O(1)] trigonal prismatic geometry. The Ba–O (disiloxane) distances for Ba(1) fall in the range 2.69(1) to 2.82(1) Å for the atoms that define the trigonal prism [O(11), O(13), O(12a) and O(11a), O(12), O(13)] and 3.14(1) Å to the edge bridging

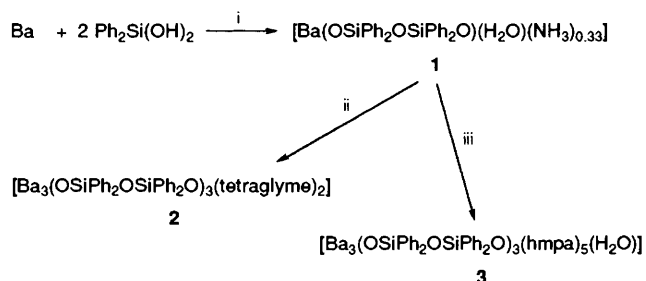
‡ IR of **1** (Nujol mull, ν/cm<sup>-1</sup>): 3380w, 3340w, br, 1429m, 1120s, 1027m. <sup>1</sup>H NMR [270 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 0.41 (s, NH<sub>3</sub>), 3.21 (s, H<sub>2</sub>O), 6.97 (m, *p*-Ph), 7.05 (m, *m*-Ph), 7.50 (d, *o*-Ph). <sup>13</sup>C NMR [67.9 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ, 126.4 (s, *p*-Ph), 126.7 (s, *m*-Ph), 134.6 (s, *o*-Ph), 144.6 (s, *i*-Ph). <sup>29</sup>Si NMR [53.6 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ -51.28 (s).

IR of **2** (Nujol mull, ν/cm<sup>-1</sup>): 2923s, 2853s, 1113m, 1031m, 1007m. <sup>1</sup>H NMR [270 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 3.23 (s, Me), 3.46 (m, CH<sub>2</sub>), 3.51 (s, CH<sub>2</sub>), 6.98 (m, *p*-Ph), 7.22 (m, *m*-Ph), 7.61 (m, *o*-Ph). <sup>13</sup>C NMR [67.9 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 58.1 (s, Me), 69.7 (s, CH<sub>2</sub>), 69.89 (s, CH<sub>2</sub>), 71.4 (m, CH<sub>2</sub>), 126.4 (s, *p*-Ph), 126.7 (s, *m*-Ph), 134.7 (s, *o*-Ph), 144.7 (s, *i*-Ph). <sup>29</sup>Si NMR [53.6 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ -46.9 (s).

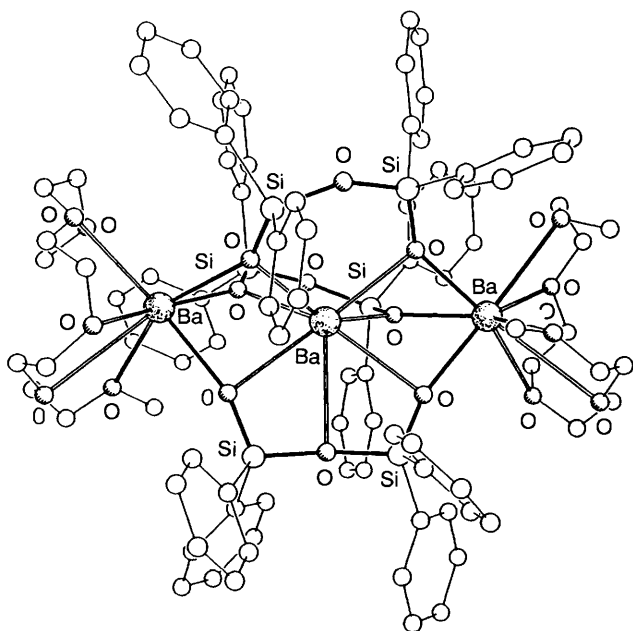
IR of **3** (Nujol mull, ν/cm<sup>-1</sup>): 3620vw, 3200w, 3131m, 3062m, 3038m, 1171s, 1012s, 983s. <sup>1</sup>H NMR [270 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 2.34 (d, NMe<sub>2</sub>), 6.65 (m, *p*-Ph), 6.85 (m, *m*-Ph), 7.39 (m, *o*-Ph). <sup>13</sup>C NMR [67.9 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 36.5 (d, NMe<sub>2</sub>), 126.3 (s, *p*-Ph), 126.9 (s, *m*-Ph), 134.7 (s, *o*-Ph), 144.7 (s, *i*-Ph). <sup>31</sup>P [109.37 MHz referenced to H<sub>3</sub>PO<sub>4</sub>, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ 25.34 (s). <sup>29</sup>Si NMR [53.6 MHz, 24 °C, (CD<sub>3</sub>)<sub>2</sub>SO] δ -51.3 (s).

§ Crystal data for [Ba<sub>3</sub>C<sub>92</sub>H<sub>104</sub>N<sub>15</sub>O<sub>19</sub>Si<sub>6</sub>] **2**: *M* = 2154.4, tetragonal, space group *P*4c2; *a* = 18.352(3), *b* = *c* = 30.771(6) Å, *Z* = 4, *D*<sub>c</sub> = 1.38 Mg m<sup>-3</sup>, *V* = 10 364(4) Å<sup>3</sup>, μ Mo-Kα = 12.6 cm<sup>-1</sup>, *F*(000) = 4360 at room temp. Of 6725 reflections collected, Mo-Kα, 4 ≤ 2θ ≤ 45°, 6343 were unique and 2990 reflections with *F*<sub>o</sub> > 5σ(*F*<sub>o</sub>) were used in the full-matrix least-squares refinement leading to the residuals *R* = 0.060 and *R*<sub>w</sub> = 0.056.

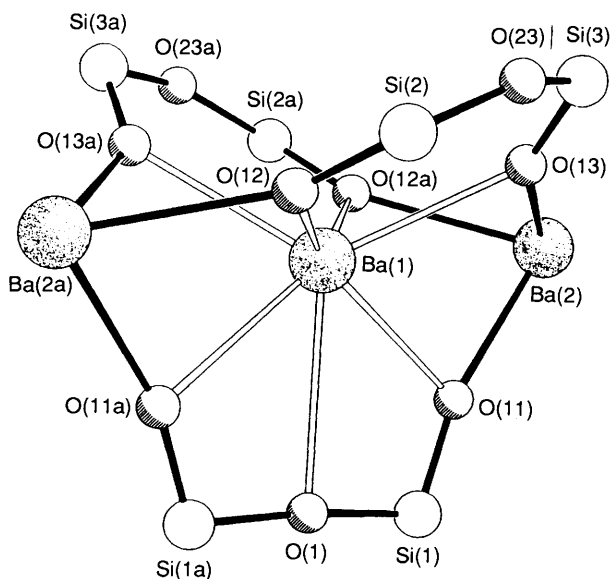
† All reactions were carried out under a dry nitrogen atmosphere in dried and carefully deoxygenated solvents. **1**: toluene (20 ml) and Ph<sub>2</sub>Si(OH)<sub>2</sub> (2.16 g, 10 mmol) were added to Ba metal turnings (0.69 g, 5 mmol) in a Schlenk tube. The reaction mixture was then cooled to -40 °C, and gaseous NH<sub>3</sub> was bubbled in for 10 min to give a light-brown suspension. When left to warm up over 1 h the mixture gave a light-purple solution. Application of a small amount of heat produced a clear solution and yielded the product as a white powder, which was filtered and dried *in vacuo*. Yield: 2.05 g, 97%. Correct elemental analyses were obtained for complexes **1–3**.



**Scheme 1** Reagents and conditions: i,  $\text{C}_7\text{H}_8\text{-NH}_3$  at  $-40^\circ\text{C}$  for 1 h; ii, 1 equiv. tetraglyme in  $\text{C}_7\text{H}_8$  at  $20^\circ\text{C}$ ; iii, 2 equiv. hmpa in  $\text{C}_7\text{H}_8$  at  $20^\circ\text{C}$



**Fig. 1** Molecular structure of complex  $[\text{Ba}_3(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3(\text{tetraglyme})_2]$  **2**, hydrogen atoms have been omitted for clarity



**Fig. 2** Structure of central  $\text{Ba}_3\text{O}_7$  core of complex **2** showing the atom numbering scheme

oxygen O(1).<sup>†</sup> The molecule has crystallographic  $C_2$  symmetry about the Ba(1)–O(1) bond. The arrangement of the three barium atoms is non-linear, subtending at an angle of  $172.6(1)^\circ$  at Ba(1), the central barium atom being folded towards O(1). The Ba–Ba non-bonded separation is  $3.766(1) \text{ \AA}$ ; this compares with distances of  $3.83\text{--}4.15 \text{ \AA}$  in other recently characterised barium alkoxides and siloxides.<sup>6</sup>

The short Ba $\cdots$ Ba non-bonded distances are a net result of the three disiloxane strands that are arranged in such a way as to draw the barium cations closer together. This effect is offset by the substantial cationic repulsion between the barium centres. The strands that link the bariums, each comprise three oxygen and two silicon atoms arranged in a pseudo helical conformation. The upper and lower triangular faces of the trigonal prism are rotated by *ca.*  $13^\circ$  with respect to the Ba(2) $\cdots$ Ba(2a) direction to produce a propellane type geometry. There is a noticeable folding of the Si(1)–O(1)–Si(1a) bridge towards Ba(1), with an Si–O–Si angle of  $175(1)^\circ$ , whereas that between Si(2)–O(23)–Si(3) is folded away, with an Si–O–Si angle of  $151(1)^\circ$ . This suggests considerable strain in the respective six membered metal–siloxane ring systems encompassing the central Ba cation.

We believe that the absence of a symmetric bridging geometry, with the central barium being nine coordinate, and binding additionally to O(23) and O(23a) may be due to the inability of the barium centres to approach any closer to each other. The terminal barium metal centres are both eight coordinate each being bound to all five tetraglyme oxygen atoms.<sup>||</sup> The replacement of water and ammonia in the precursor complex **1** by tetraglyme is a good example of the chelate effect with elimination of all the monodentate ligands.

The crystal structure of **3**<sup>\*\*</sup> reveals the complex to have a gross structure very similar to that of **2** (Fig. 3). The two terminal tetraglyme ligands have been replaced at one terminus by three hmpa ligands and at the other by two hmpa and one water molecule (evidently retained from complex **1**). This asymmetric substitution destroys the  $C_2$  symmetry of the complex. However, the core consists of three barium atoms each bridged by six diphenylsiloxide groups with a seven coordinate central barium atom. The edge bridged trigonal prismatic geometry of the central barium atom is noticeably more distorted than that observed for **1**, the upper and lower triangular face being twisted by *ca.*  $22^\circ$  with respect to the mean Ba $\cdots$ Ba $\cdots$ Ba direction (*cf.*  $13^\circ$  in **1**). Approximate crystallographic  $C_2$  symmetry is still retained for the central

<sup>†</sup> The coordination of each terminal barium atom is severely distorted bicapped trigonal prismatic with Ba–O distances in the range  $2.55(1)\text{--}2.65(1) \text{ \AA}$  to the siloxide oxygen atoms.

<sup>||</sup> Because of the severe disorder in the polyether chains, their geometries have been optimised and refined subject to C–C and C–O distance constraints. Hence we do not consider it meaningful to discuss specifically the Ba–O<sub>(glyme)</sub> distances though they are all longer than those to the siloxide oxygen atoms.

<sup>\*\*</sup> *Crystal data* for  $[\text{Ba}_3\text{C}_{102}\text{H}_{152}\text{N}_{15}\text{O}_{15}\text{P}_{15}\text{Si}_6]\cdot\text{X}_{2.5}$  (X represents unidentified disordered solvent fragments refined as partial weight C atoms) **3**:  $M = 2593.8$ , orthorhombic space group  $Pcab$ ;  $a = 26.47(3)$ ,  $b = 30.71(2)$ ,  $c = 33.03(4) \text{ \AA}$ ,  $Z = 8$ ,  $D_c = 1.283 \text{ Mg m}^{-3}$ ,  $V = 26854(49) \text{ \AA}^3$ ,  $\mu_{\text{Mo-K}\alpha} = 10.4 \text{ cm}^{-1}$ ,  $F(000) = 10\ 648$ , and room temp. Of 12 944 reflections collected,  $\text{Mo-K}\alpha$ ,  $4 \leq 2\theta \leq 45^\circ$ , 12 527 were unique and 6486 reflections with  $F_o > 3\sigma(F_o)$  were used in the full-matrix least-squares refinement leading to the residuals  $R = 0.108$  and  $R_w = 0.122$ . The high final values for  $R$  are due to decomposition of the crystal during data collection, severe disorder in some of the phenyl rings and hmpa methyl groups, and the ability to refine only the Ba, Si and P atoms anisotropically owing to the shortage of observed data. The core structure is definitively determined however. Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

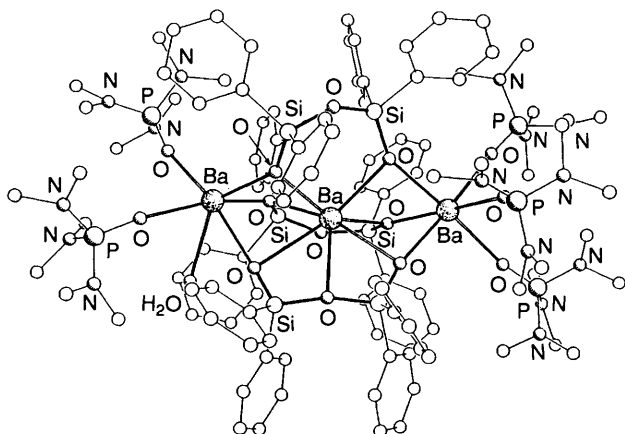


Fig. 3 Molecular structure of complex  $[Ba_3(OSiPh_2OSiPh_2O)_3-(hmpa)_5(H_2O)]$  **3**, hydrogen atoms have been omitted for clarity

core. The unusual pattern of the folding of one Si–O–Si bridge towards the central barium atom [Si–O–Si angle =  $164.3(14)^\circ$ ] with the other two folded away [Si–O–Si angles  $146.2(14)$  and  $152(15)^\circ$ , respectively] is repeated. The Ba...Ba non-bonded separations are  $3.781(5)$  and  $3.809(5)$  Å, respectively, with an angle of  $167.0(1)^\circ$  subtended at the central barium atom. The direction of fold is again towards the edge capping oxygen associated with the inwardly directed Si–O–Si bridge with a Ba–O distance of  $3.00(1)$  Å.

Coordination geometries at the terminal barium centres in **3** are both essentially octahedral though that which is coordinated to two hmpa ligands and one water molecule is severely distorted.<sup>††</sup> This distortion may be due to the formation of an intramolecular hydrogen bond between the water molecule and the oxygen atom of the adjacent Ba–O–Si bridge [O...O separation =  $2.60(5)$  Å].<sup>‡‡</sup> There is a noticeable lengthening of the distance of this oxygen to the central Ba atom compared to that of the other equivalent coordinated oxygens [Ba–O distance =  $2.96(2)$  Å, *cf.* range of  $2.67$ – $2.75$  Å for other

<sup>††</sup> At the barium centre with three hmpa ligands the angles at Ba are in the ranges *ca.*  $77$ – $100$  and  $170$ – $177^\circ$  whilst at the other terminal Ba atom the angles at barium are in the ranges  $50$ – $130$  and  $133$ – $163^\circ$ , respectively.

<sup>‡‡</sup> Although the O...O separation is strongly indicative of an hydrogen bonding interaction the protons were not located and thus a definitive assignment hydrogen of the H bond cannot be made.

oxygens that define the trigonal prism]. In the structures of **1** and **2** there is an absence of any major intermolecular interactions; indeed both molecules have essentially spherical hydrophobic exteriors.

The reaction of monodentate Lewis bases (*e.g.* hmpa) with the precursor complex **1**, has surprisingly shown that although the  $NH_3$  is easily substituted, the  $H_2O$  ligand is a good match for the barium centre. Therefore our strategy of using a multidentate ligand in the presence of the siloxane ligand, and mixtures of alkaline earth metals and or Yb or Eu (both of these metals are known to dissolve in liquid ammonia) are currently being explored.

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