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# Triorganosiloxy and tetraphenyldisiloxydiolate complexes of the heavier alkaline-earth metals. Crystal structures of $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) and $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ [tetraglyme = $CH_3O(CH_2CH_2O)_4CH_3$]†

**Ian Baxter,[a] Jawwad A. Darr,[b] Simon R. Drake,[b] Michael B. Hursthouse,*,[a] K. M. Abdul Malik[a] and D. Michael P. Mingos*,[b]**

[a] *Department of Chemistry and Applied Chemistry, University of Wales Cardiff, PO Box 912, Park Place, Cardiff, UK CF1 3TB*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY*

Strontium or barium metal granules reacted with an excess of $HOSiMe_2Bu^t$ in an ammoniacal toluene solution at −40 °C to produce the corresponding $[M(OSiMe_2Bu^t)_2]_n$. The strontium complex was also obtained from silanolysis of the strontium ethoxide $[\{Sr(OEt)_2(HOEt)_4\}_n]$ with an excess of $HOSiMe_2Bu^t$ in hot toluene solution. Similarly, the reaction of $[\{Sr(OEt)_2(HOEt)_4\}_n]$ in hot toluene, with 1 molar equivalent of $HOSiPh_3$ and Htmhd (2,2,6,6-tetramethylheptane-3,5-dione) yielded the trimeric complex $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$. The reaction of strontium or barium metal granules with 2 molar equivalents of diphenylsilanediol $[Ph_2Si(OH)_2]$ in ammoniacal toluene solution at −40 °C yielded the polymeric complexes $[\{M[O(SiPh_2O)_2](H_2O)(NH_3)_x\}_n]$ [M = Ca ($x$ = 0.3), Sr ($x$ = 1) or Ba ($x$ = 0.3)]. Similar reactions for strontium and barium in the presence of an excess of hmpa $[OP(NMe_2)_3]$ produced $[Sr_3\{O(SiPh_2O)_2\}_3(hmpa)_5]\cdot C_6H_5Me$ and $[Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)]$, respectively. Alternatively, when these reactions were performed in the presence of tetraglyme $[CH_3O(CH_2CH_2O)_4CH_3]$ the water- and $NH_3$-free complexes $[M_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ were obtained (M = Sr or Ba). All complexes have been characterised by elemental analyses and IR, NMR ($^1H$, $^{13}C$ and $^{29}Si$, in selected cases $^{31}P$) spectroscopy and also by TGA/DSC studies. The complexes $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$ and $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ have been characterised by X-ray crystallography. The structure of the former reveals a trimer of strontium cations stabilised by three tmhd ligands, and one μ- and two $\mu_3$-bridging triphenylsiloxy ligands. Relatively short Sr · · · C (methyl) and Sr · · · C (phenyl) contacts have also been identified in this compound. In contrast, the three strontium cations in the latter are arranged in an almost linear array within a $Sr_3O_9Si_6$ core.

Metal oxides and silicates have found wide ranging applications from paint modifiers[1] to catalysts in a range of industrially important processes.[2] Structural and mechanistic studies in such important systems are, however, poorly defined due to the generally low solubilities of the compounds in hydrocarbon solvents. Low-molecular-weight, hydrocarbon-soluble triorganosiloxy and tetraorganodisiloxydiolate compounds have attracted much interest because it is hoped that they may mimic the reaction chemistry of metal oxides bonded to silica. Important reaction intermediates in such systems can be characterised by structural studies and in solution using spectroscopic methods (NMR, IR, *etc.*). These compounds also have potential as molecular precursors to the respective metal oxides/silicates *via* either sol-gel (controlled hydrolysis) or chemical vapour deposition (CVD) techniques.[3]

The preparation of many related Group 1 and 2 alkoxides has been achieved by the reaction of the respective metals with an excess of alcohol.[4] However, the Group 2 metals (Ca to Ba) failed to react with various silanols under identical conditions.[5,6] Some success was, however, achieved by utilising 'Rieke' metal powders and metal vapour synthesis (MVS) techniques.[7,8] Miscellaneous reactions for the synthesis of M−O−Si linkages (where M = Group 2 metal) include the silanolysis of dimethylberyllium to give the cubane compound $[BeMe(OSiMe_3)]_4$,[9] whilst the reaction of $MgBu^n_2$ with an excess of $HOSiMe_2Bu^t$ yielded the silanol-adducted complex $[Mg(OSiMe_2Bu^t)_2(HOSiMe_2Bu^t)]$.[6] It was also observed that the reaction of $Me_3SiO(CH_2)_3Cl$ and magnesium gave $MgCl(OSiMe_3)$ and $C_3H_6$.[10] Whilst the reaction of $[Mg(CH_2SiMe_3)\{HB(bpz)_3\}]$ (bpz = 3-*tert*-butylpyrazolyl) with molecular oxygen led to facile cleavage of the Si−C bonds and formation of $[Mg\{HB(bpz)_3\}(OSiMe_3)]$ (and formaldehyde) rather than the expected insertion product.[11] More recently, solubilisation and activation of the heavier Group 2 metals (Ca, Sr, Ba) has been achieved by dissolving the metals in ammonia–hydrocarbon solvent mixtures at low (−40 °C) or room temperatures.[5,6,12–15] This method has provided a viable route to the synthesis of new Group 2 complexes that were previously inaccessible by the reaction of the metal and organic ligand (silanol). However, the ammoniacal reaction mixtures are at times problematical and alternative routes which do not involve ammoniation are desirable.

To date, there have been relatively few reports of well characterised, hydrocarbon-soluble aggregates involving tetraorganodisiloxydiolate complexes of the alkaline-earth metals. These include $[Ba\{O(SiMe_2O)_2\}\{O(SiMe_2O)_3\}(py)_3\{Y(tmhd)_2\}_2]$ (H-tmhd = 2,2,6,6-tetramethylheptane-3,5-dione, py = pyridine)[16] and $[Mg\{O(SiPh_2O)_2\}\{O(SiPh_2O)_3\}\{Li(py)_2\}_2]$.[17] The unusual 'one pot' synthesis of the former compound was achieved by treating barium metal and $[Y_5O(OPr^i)_{13}]$ with Htmhd

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† *Non-SI unit employed*: Torr ≈ 133 Pa.

$$\mathrm{Ba} + 2\ \mathrm{Ph_2Si(OH)_2} \xrightarrow{\mathrm{C_6H_5Me,\ NH_3,\ -40\ ^\circ C}} [\{\mathrm{Ba[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}}\}_n]$$

Scheme 1

$$[\{\mathrm{Sr(OEt)_2(HOEt)_4}\}_n] + \underset{\text{excess}}{\mathrm{HOSiMe_2Bu^t}} \xrightarrow{\mathrm{C_6H_5Me,\ heat}} [\mathrm{Sr(OSiMe_2Bu^t)_2}]_n + 6\ \mathrm{HOEt}$$

**1**

Scheme 2

$$3\ [\{\mathrm{Sr(OEt)_2(HOEt)_4}\}_n] + 3\ \mathrm{HOSiPh_3} + 3\ \mathrm{Htmhd} \xrightarrow{\mathrm{C_6H_5Me,\ heat}} [\mathrm{Sr_3(tmhd)_3(OSiPh_3)_3}]\cdot 0.5\mathrm{C_6H_5Me} + 18\ \mathrm{HOEt}$$

**3**

Scheme 3

in toluene, followed by recrystallisation from a mixture of toluene–pyridine and siloxane derivatives.[16] In contrast, the magnesium *spiro*-complex $[\mathrm{Mg\{O(SiPh_2O)_2\}\{O(SiPh_2O)_3\}\{Li(py)_2\}_2}]$ was obtained in low yield *via* the reaction of $\mathrm{MgCl_2}$ with $[\mathrm{Li_2(OSiPh_2OSiPh_2O)}]_n$ in the presence of pyridine.[17] We also reported in an earlier communication the high-yield condensation reaction of $\mathrm{Ph_2Si(OH)_2}$ ligands in an ammoniacal toluene–barium metal mixture to give $[\{\mathrm{Ba[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}}\}_n]$ (Scheme 1).[18] The addition of an excess of tetraglyme $[\mathrm{CH_3O(CH_2CH_2O)_4CH_3}]$ or hmpa $[\mathrm{OP(NMe_2)_3}]$ to a toluene suspension of this complex, afforded crystals of $[\mathrm{Ba_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2}]\cdot 0.5\mathrm{C_6H_5Me}$ and $[\mathrm{Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)}]$ respectively.[18] These oligomers are based on a $[\mathrm{Ba_3\{O(SiPh_2O)_2\}_3}]$ core, which is extremely stable in the presence of very strongly co-ordinating Lewis bases or multidentate ligands. This contrasts to the related Group 2 triorganosiloxy-complexes, which can form monomeric species upon co-ordination of neutral coligands.[6,15]

We have sought to develop new strategies for the syntheses of Group 2 triorganosiloxy and tetraphenyldisiloxydiolate complexes using synthetic routes which are well established for the preparation of other metal derivatives.

## Results and Discussion

### Synthesis and physical properties

The respective reactions of Sr and Ba metals with 2 or more molar equivalents of $\mathrm{HOSiMe_2Bu^t}$ in ammoniacal toluene gave products containing weakly solvated ammonia molecules. Mild heating of the solutions in each case caused reversible loss of all solvated ammonia and precipitation of the homoleptic siloxy-compounds $[\mathrm{M(OSiMe_2Bu^t)_2}]_n$ (M = Sr **1** or Ba **2**). Alternatively, refluxing strontium ethoxide $[\{\mathrm{Sr(OEt)_2(HOEt)_4}\}_n]$ in a toluene solution of an excess of $\mathrm{HOSiMe_2Bu^t}$ gave the corresponding homoleptic complex $[\mathrm{Sr(OSiMe_2Bu^t)_2}]_n$ **1** after removal of all volatiles (Scheme 2). Attempts to prepare crystalline Lewis-base adducts of complex **1** gave powdered complexes with no or minimum Lewis-base incorporation.[6]

Recently, we have prepared many Group 2 mixed alkoxide–β-diketonate complexes *via* the corresponding Group 2 ethoxides.[19] Refluxing a toluene solution of crystalline strontium ethoxide with equimolar amounts of Htmhd and $\mathrm{HOSiPh_3}$ led to completion of the reaction within minutes. Removal of all volatiles (including the liberated ethanol) and recrystallisation from a hot toluene solution gave the complex $[\mathrm{Sr_3(tmhd)_3(OSiPh_3)_3}]\cdot 0.5\mathrm{C_6H_5Me}$ **3** (Scheme 3).

$$3\ [\{\mathrm{Sr[O(SiPh_2O)_2](H_2O)(NH_3)}\}_n] + 2\ \mathrm{L{-}L} \xrightarrow{\mathrm{C_6H_5Me,\ heat}} [\mathrm{Sr_3\{O(SiPh_2O)_2\}_3(L{-}L)_2}]\cdot 0.5\mathrm{C_6H_5Me} + 3\mathrm{H_2O} + 3\mathrm{NH_3}$$

**5** **9**

Scheme 4

The syntheses of the lightly stabilised tetraphenyldisiloxydiolate compounds $[\{\mathrm{M[O(SiPh_2O)_2](H_2O)(NH_3)_x}\}_n]$ [M = Ca **4** ($x = 0.3$), Sr **5** (1.0) or Ba **6** (0.3)], resulted from the condensation reactions of diphenylsilanediol $[\mathrm{Ph_2Si(OH)_2}]$ in ammoniacal toluene–metal (Ca, Sr or Ba) mixtures at −40 °C (metal : ligand ratio 1 : 2). Overall, the reactions produced 1 molar equivalent of water [per two $\mathrm{Ph_2Si(OH)_2}$ ligands], which could then co-ordinate to the polymerised product in the absence of stronger or more accessible donor ligands. An analogous 'chain expansion' was observed in the synthesis of $[\{\mathrm{Ti[O(SiPh_2O)_3]_2(py)_2}\}_n]$ from the reaction of $[\mathrm{Li_2\{O(SiPh_2O)_2\}}]_n$ and $\mathrm{TiCl_4}$, followed by recrystallisation from a pyridine–benzene mixture.[20,21] It was believed that the mechanism for ring expansion of the lithium precursor to the product may have proceeded *via* attack of a silonate anion ($^-$OSi) on a Si or Ti atom. A stepwise chain-expansion mechanism was proposed for the formation of $[\mathrm{Ti\{O(SiPh_2O)_4\}_2}]$ which was synthesized from the reaction of $\mathrm{Ph_2Si(OH)_2}$ with $\mathrm{TiBu^n{}_4}$.[21]

As expected, the metal dissolution rates in ammoniacal toluene generally decreased from barium to calcium. Even in very dilute ammoniacal solutions it was possible to complete the reaction for compound **6** in *ca.* 2 h. However, concentrated ammoniacal toluene solutions were employed as the reaction times were considerably shorter. Complexes $[\mathrm{Sr_3\{O(SiPh_2O)_2\}_3(hmpa)_5}]\cdot\mathrm{C_6H_5Me}$ **7**, $[\mathrm{Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)}]$ **8** and $[\mathrm{M_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2}]\cdot 0.5\mathrm{C_6H_5Me}$ (M = Sr **9** or Ba **10**) were synthesized in metal–ammoniacal toluene mixtures containing an excess of either hmpa or tetraglyme and obtained as colourless crystals. The reactions leading to **4** and **5** were also conducted in a 2 : 1 molar ratio of $\mathrm{Ph_2Si(OH)_2}$ to metal. Our repeated attempts to stabilise these compounds using only 1 molar equivalent of diphenylsilanediol with respect to metal yielded large amounts of unreacted metal or metal amide in the reaction mixtures.

The toluene reflux method was used as an alternative route for the syntheses of complexes **7**–**10**. For example, **7** and **9** were synthesized by the slow addition, respectively, of hmpa and tetraglyme (L−L) to the ammonia/water adduct $[\{\mathrm{Sr[O(SiPh_2O)_2](H_2O)(NH_3)}\}_n]$ **5** in refluxing toluene (Scheme 4). Completion of the respective reactions was suggested by the solubilisation of the reactants after a few minutes.

Complexes **1** and **2** were very soluble in dmso (dimethyl sulfoxide) and pyridine and showed poor solubilities in toluene, benzene and *n*-hexane, whilst compounds **3**–**10** were soluble in a range of co-ordinating solvents and showed poor to moderate solubilities in non-co-ordinating solvents such as benzene and *n*-hexane. Crystals of compounds **7**–**10** gave opaque solids on exposure to air for a few minutes. Compounds **1**–**3** were extremely air and moisture sensitive, whilst **4**–**6** slowly lost some co-ordinated ammonia whilst stored in a glove-box for a few weeks. Sublimation studies for **4**–**7** revealed that the compounds did not sublime. Infrared studies of the unsublimed residues suggested that the corresponding homoleptic compounds had been obtained.

### Infrared spectra

The IR spectra were obtained as either Nujol and/or hexachlorobutadiene (hcb) mulls, with samples prepared inside an inert-atmosphere glove-box. Those for complexes **1**–**3** did not contain any peaks above 3270 $\mathrm{cm^{-1}}$, suggesting the absence of any water and/or ammonia molecules in these compounds. In contrast, the spectra for **4**–**6** revealed up to three sharp peaks in the range 3484–3295 $\mathrm{cm^{-1}}$, which were assigned to the ν(N−H) stretching modes of co-ordinated ammonia (*cf.* N−H stretching modes have previously been reported at 3373, 3380 and 3414 $\mathrm{cm^{-1}}$).[6,14,15] Additionally, the IR spectra for **4**, **5**, **6** and **8** con-

**Table 1** The ν(Si–O)X (X = metal or Si), ν(N–H) and ν(O–H) IR stretching frequencies ($cm^{-1}$) for complexes **4**–**6** and **8**

| | | | | ν(O–H) | | |
|---|---|---|---|---|---|---|
| Complex | Solvent | ν(Si–O)X | ν(N–H) | free | co-ordinated | Ref. |
| **4** $[\{Ca[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}\}_n]$ | hcb | 1117s, 1045s, 1032s, 1015s | 3484vw, 3372vw, 3295vw | 3646w | 3300 (br) | * |
| **5** $[\{Sr[O(SiPh_2O)_2](H_2O)(NH_3)\}_n]$ | Nujol | 1117s, 993s | 3380vw | 3620vw | 3300 (br) | * |
| | hcb | 1110s | 3383 (br) | 3621vw | 3200w | * |
| **6** $[\{Ba[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}\}_n]$ | Nujol | 1120s, 1027m | 3380w | — | 3340w | 18,* |
| | hcb | 1119s, 1051s | 3380w | 3627w, 3545vw | *ca.* 3380w (br) | * |
| **8** $[Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)]$ | Nujol | 1012s | — | 3620vw | 3200w | 18,* |
| | hcb | 1111s, 1012s | — | 3624vw | 3171 (br) | * |

* This work. s = Strong, m = medium, w = weak, v = very, br = broad.

**Table 2** Proton NMR chemical shifts (δ, *J*/Hz) for complexes **4**, **5**, **7** and **9** in different solvents

| | | Ph | | | |
|---|---|---|---|---|---|
| Compound | Solvent | *o*-H | *p*-, *m*-H | Neutral ligands | $C_6H_5CH_3$ |
| **4** | $C_5D_5N$ | 7.87 (d) | 7.26 (m) | 5.20 (br, $H_2O$), 0.79 (br, $NH_3$) | — |
| **5** | $C_5D_5N$ | 7.90 (d) | 7.19 (m) | 5.15 (w, $H_2O$), 0.55 (w, $NH_3$) | — |
| **7** | $C_6D_6$ | 7.96 (d) | 7.09 (m, also $C_6H_5Me$) | 2.16 (d, hmpa $CH_3$) | 2.09 |
| | $C_5D_5N$ | 7.86 (d) | 7.16 (m, also $C_6H_5Me$) | 2.43 (d, hmpa $CH_3$) | 2.20 |
| **9** | $C_5D_5N$ | 7.80 (d) | 7.16 (m, also $C_6H_5Me$) | 3.63, 3.50 (glyme $CH_2$), 3.25 (glyme $CH_3$) | 2.22 |

All peaks are singlets unless stated otherwise: d = doublet, m = multiplet, w = weak, br = broad.

**Table 3** Carbon-13 NMR chemical shifts (δ, *J*/Hz) for complexes **4**, **5**, **7** and **9** in different solvents and in the solid state

| | | Ph | | | | |
|---|---|---|---|---|---|---|
| Compound | Solvent | *ipso*-C | *o*-C | *m*-C | *p*-C | Neutral ligands |
| **4** | $C_5D_5N$ | 143.6 | 136.1 | 128.2 | 127.5 | — |
| **5** | $C_5D_5N$ | 144.3 | 135.7 | 130.6 | 128.5 | — |
| | Solid state[a] | 141.2 | 136.2 | 127.7 (br, m) | 127.7 (br, m) | — |
| **7**[c] | $C_6D_6$ | 145.1 | 136.1 | 128.0[b] | 127.0 | 36.6 (d, hmpa $CH_3$) |
| | $C_5D_5N$ | 144.6 | 136.1[b] | 127.6 | 127.3 | 37.0 (d, hmpa $CH_3$) |
| **9**[c] | $C_5D_5N$ | 144.0 | 135.8 | 128.0 | 127.4 | 72.3, 71.0, 70.8 (glyme $CH_2$), 58.7 (glyme $CH_3$) |

All peaks are singlets unless stated otherwise. [a] CP MAS NQSTOSS (non-quatenary suppression, total sideband suppression). [b] Peak is obscured by the protio impurity contained in the deuteriated solvent. [c] Spectrum also contains peaks due to toluene phenyl and methyl hydrogens in the expected positions.

tained broad bands in the range *ca.* 3340–3171 $cm^{-1}$ which were attributed to ν(O–H) stretching modes of co-ordinated water. Some of these spectra also contained a weak signal at *ca.* 3620 $cm^{-1}$ due to ν(O–H) stretches of free or residual water (Table 1). The IR spectra (Nujol) for complexes **7** and **8** revealed peaks which were indicative of P=O (1197 $cm^{-1}$ for **7**), C–N (1171 $cm^{-1}$ for **8**) and P–N (987 and 742 $cm^{-1}$ for **7**, 983 and 743 $cm^{-1}$ for **8**) stretching vibrations of hmpa (Experimental section).[6,18]

Infrared spectra for complexes **1**–**3** showed bands in the region 1030–910 $cm^{-1}$, which were assigned to the ν(Si–O)M stretching modes.[6,14,15,22] Similarly, spectra for **4**–**10** contained peaks in the range *ca.* 1120–993 $cm^{-1}$ due to ν(Si–O)X (X = metal or Si) stretching frequencies (see Table 1 and Experimental section).[1,6]

## Nuclear magnetic resonance spectra

Proton and $^{13}C$-$\{^1H\}$ NMR solution spectroscopy for complexes **1**–**10** revealed only single time-averaged ligand signals (see Tables 2 and 3 for $^1H$ and $^{13}C$-$\{^1H\}$ NMR data of complexes **4**, **5**, **7** and **9**). The respective $^1H$ NMR spectra for **4**–**6** revealed a single peak due to N–H hydrogen (from co-ordinated $NH_3$) resonances in the range δ 0.4–0.79. Additionally, broad signals in the range δ 5.2–3.2 due to co-ordinated water (OH) hydrogens were observed (Table 2).[6,18]

The respective $^{29}Si$-$\{^1H\}$ NMR solution spectra of complexes **1** and **2** revealed two resonances separated by *ca.* δ 7.2. These peaks were located considerably upfield of the shift which is associated for the corresponding free silanol (δ 17.5). It is possible that, despite time-averaging effects, resolution of bridging and terminal environments in solution was being observed in the $^{29}Si$-$\{^1H\}$ NMR spectra for complexes **1** and **2**. Alternatively, as a result of the co-ordination of deuteriated dmso, a mixture of products is obtained in solution. Only one signal was observed in the $^{29}Si$-$\{^1H\}$ NMR spectrum for **3**.

The respective $^{29}Si$-$\{^1H\}$ NMR solution spectra for complexes **4**, **5** and **6** in co-ordinating solvents revealed single peaks at δ −46.3, −47.2 and −51.3 respectively, substantially upfield of free $Ph_2Si(OH)_2$ (δ −34.9).[6] Assuming these complexes are trimeric and retain this arrangement in co-ordinating solvents (as suggested from the crystal structures of compounds **8**–**10**), these differences in chemical shift can be attributed to the increased shielding effect on the Si atoms from Ca to Ba. In contrast to the solution spectra, the solid-state $^{29}Si$-$\{^1H\}$ NMR spectra were far more revealing (Table 4). Seven distinct peaks were observed in the spectrum for compound **8**, whilst three peaks (in the ratio of 1 : 4 : 1) were observed in the corresponding spectrum for **7**. These results are consistent with unequal silicon environments as observed in the solid-state structures of the barium and strontium tetraphenyldisiloxydiolate cores (*cf.* compounds **8**, **9** and **10**).[6,18]

The $^{31}P$-$\{^1H\}$ NMR solution spectra for complexes **7** and **8** revealed only one type of $^{31}P$ environment for the hmpa ligands, whilst the solid-state $^{31}P$-$\{^1H\}$ NMR spectrum for **8** showed

**Table 4** Silicon-29 Si NMR chemical shifts (δ, *J*/Hz) for complexes **1–10** in range of different solvents and in the solid state

| Compound | Solvent | | | Solid state | Ref. |
|---|---|---|---|---|---|
| | $C_6D_6$ | $(CD_3)_2SO$ | $C_5D_5N$ | | |
| **1** $[Sr(OSiMe_2Bu^t)_2]_n$ | — | −5.9, −13.1 (1:3) | — | — | *a* |
| **2** $[Ba(OSiMe_2Bu^t)_2]_n$ | — | −4.6 (br), −9.0 (br) (1:3) | — | — | *a* |
| **3** $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot 0.5C_6H_5Me$ | — | −13.0 | — | — | *a* |
| **4** $[\{Ca[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}\}_n]$ | — | — | −46.3 | −44.4 (s, br)[b] | *a* |
| **5** $[\{Sr[O(SiPh_2O)_2](H_2O)(NH_3)\}_n]$ | — | — | −47.2 | −43.2, −46.0, −48.1 (w)[b] | *a* |
| **6** $[\{Ba[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}\}_n]$ | — | −51.3 | — | — | 18,[a] |
| **7** $[Sr_3\{O(SiPh_2O)_2\}_3(hmpa)_5]\cdot C_6H_5Me$ | −48.9 | — | — | −47.2, −49.6, −50.7 (1:4:1)[b] | *a* |
| **8** $[Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)]$ | −50.4 | −51.3 | — | −46.0 to −50.7 (7 peaks)[b] | 18,[a] |
| **9** $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ | — | — | −47.9 | — | *a* |
| **10** $[Ba_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ | — | −46.9 | — | — | 18,[a] |

[a] This work. [b] CP MAS (cross polarisation magic-angle spinning).

three peaks at δ 24.73, 23.36 and 22.74, suggesting that inequivalent hmpa ligand environments exist in the solid state (see Experimental section).

## TGA and DSC studies

The TGA and DSC measurements on selected complexes were obtained under a constant flow of dry nitrogen. The TGA/DSC plots for the homoleptic complexes $[M(OSiMe_2Bu^t)_2]_n$ (M = Sr **1** and Ba **2**) were extremely complicated and suggested many distinct weight-loss stages. Both TGA plots revealed small weight-loss regions below 110 °C, which were attributed to residual solvent loss from the compounds. The major regions of weight loss for compounds **1** and **2** are summarised as follows: $[Sr(OSiMe_2Bu^t)_2]_n$ **1**, (*i*) 30–110 °C, *ca.* 1% weight loss due to residual solvent; (*ii*) 170–340 °C, decomposition; (*iii*) 340–382 °C, exotherm at 383 °C; (*iv*) 382–1000 °C, slight weight loss, weak exotherm at 770 °C; final residue at 1000 °C, 55.1% [metal oxide (MO) would be expected to give a residue of 29.7%]; $[Ba(OSiMe_2Bu^t)_2]_n$ **2**, (*i*) 21.0–68.4 °C, 1.5% weight loss due to residual solvent, endotherm at 60.4 °C; (*ii*) 68.4–480.9 °C, decomposition, endotherm at 476.7 °C; (*iii*) 476.7–1000 °C, slight weight loss; final residue at 1000 °C, 47.9% [metal oxide (MO) would be expected to give a residue of 38.3%].

Unlike the corresponding copper(I) siloxy-complexes, which thermally decomposed to the elemental metal,[23] the above Group 2 metal compounds decomposed to give relatively large residues at 1000 °C, which suggested the presence of substantial siliceous and/or carbonaceous material. Although mass spectrometric investigations for complexes **1** and **2** were performed independently of the TGA analyses, they did give some indication of likely volatile degradation products.[6] These included free silanol as well as substantial polysiloxane chains based on '$(OSiR_x)_n$' (R = Me or $Bu^t$) molecular units in the gas phase.[6] This is not surprising when the strength and stability of the Si–O bonds is considered.

The TGA curve for $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot 0.5C_6H_5Me$ **3** revealed a small weight loss (*ca.* 2%) from 25 to 167 °C, attributed to the small amount of toluene solvent (expected loss 2.4%). The remaining regions of weight loss were not as well defined, however the DTG (first derivative) curve suggested at least three additional regions. These were between (*i*) 275 and 328, (*ii*) 328 and 379 and (*iii*) 389 and 440 °C respectively (associated with very weak exotherms). At higher temperatures slow weight loss due to further decomposition was suggested (29.0% residue at 550, 22.7% at 600 °C) in the TGA spectrum, giving a final residue of 17.6% at 900 °C [expected for metal oxide (MO) 18.6%]. The TGA curve for compound **3** can be contrasted to that of $[Sr_3(tmhd)_6(Htmhd)]$, which almost completely sublimed by 400 °C (residue of 3–4%).[24]

The TGA plot for $[\{Sr[O(SiPh_2O)_2](H_2O)(NH_3)\}_n]$ **5** revealed substantial weight losses at lower temperatures due to the removal of co-ordinated water, ammonia and any residual water or solvent to give $\{Sr[O(SiPh_2O)_2]\}_n$ which subsequently underwent decomposition at higher temperatures. The first-derivative plot of the TGA clearly identified at least two major overlapping reactions between (*i*) 100 and 260 and (*ii*) 260 and 605 °C. The first reaction resulted in an observed weight loss of *ca.* 8% (calculated 5.8%). The higher than expected weight loss in this temperature range was attributed to residual water and/or solvent which was present. The nature of the second reaction was less clearly understood, although it possibly involved the loss of the phenyl groups and/or polysiloxane chains. This reaction was also supported by the presence of at least one endotherm in the DSC curve, which was centred at *ca.* 300 °C.

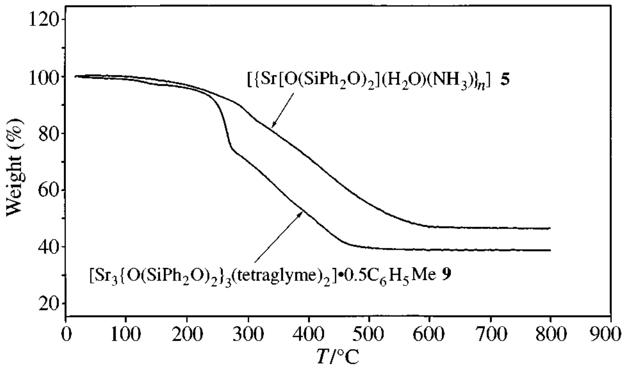

**Fig. 1** Thermogravimetric analysis plots for $[\{Sr[O(SiPh_2O)_2](H_2O)(NH_3)\}_n]$ **5** and $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ **9**

The TGA graph and DTG plots for $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ **9** suggested at least three major overlapping reactions between (*i*) 25 and 120, (*ii*) 150 and 270 and (*iii*) 270 and 500 °C. The first process is consistent with expulsion of the toluene solvent (observed loss 3%, calculated 2.3%). The DSC curve revealed a sharp endotherm at 265 °C due to expulsion of all tetraglyme from the complex (corresponding to the second reaction; observed weight loss of 22%, calculated 22.8%). The nature of the third reaction was less clearly understood, although it possibly involved the loss of the phenyl groups and/or polysiloxane chains. The weight of the final residue (38.5%) was much higher than expected for metal oxide only (calculated 16%). It was observed that the final residues obtained for complexes **5** (46.2) and **9** (38.5%) both corresponded to *ca.* 49% of the total mass of the homoleptic compound '$\{Sr[O(SiPh_2O)_2]\}_n$' (based on the suggested formulae for the respective complexes). This suggests that after the loss of the neutral Lewis-base ligands these compounds have comparable decomposition patterns at higher temperatures (Fig. 1).

## Mass spectrometry

The air-sensitive and involatile nature of many of the complexes prevented any metal-containing species being observed

**Table 5** Selected interatomic distances (Å) and angles (°) for $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot 0.5C_6H_5Me$ **3**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sr(1)–O(2) | 2.384(3) | Sr(1)–O(9) | 2.436(3) | Sr(3)–O(9) | 2.440(3) | Sr(3)–O(5) | 2.441(3) |
| Sr(1)–O(7) | 2.496(3) | Sr(1)–O(8) | 2.541(3) | Sr(3)–O(7) | 2.628(3) | Sr(3)–O(8) | 2.636(3) |
| Sr(1)–O(1) | 2.627(3) | Sr(1)···C(81) | 3.305(5) | Sr(3)–O(4) | 2.646(3) | Sr(1)···Sr(2) | 3.544(2) |
| Sr(2)–O(3) | 2.347(3) | Sr(2)–O(8) | 2.469(3) | Sr(1)···Sr(3) | 3.567(1) | Sr(2)···Sr(3) | 3.654(2) |
| Sr(2)–O(7) | 2.477(3) | Sr(2)–O(1) | 2.503(3) | O(1)–C(2) | 1.289(5) | O(2)–C(4) | 1.258(5) |
| Sr(2)–O(4) | 2.542(3) | Sr(2)···C(45) | 3.105(5) | O(3)–C(13) | 1.260(5) | O(4)–C(15) | 1.291(5) |
| Sr(2)···C(6) | 3.195(5) | Sr(3)–O(6) | 2.404(3) | O(5)–C(24) | 1.271(5) | O(6)–C(26) | 1.276(5) |
| O(2)–Sr(1)–O(9) | 140.48(11) | O(2)–Sr(1)–O(7) | 136.71(10) | O(9)–Sr(3)–O(7) | 75.80(9) | O(5)–Sr(3)–O(7) | 161.08(10) |
| O(9)–Sr(1)–O(7) | 78.37(10) | O(2)–Sr(1)–O(8) | 122.66(11) | O(6)–Sr(3)–O(8) | 164.05(9) | O(9)–Sr(3)–O(8) | 78.17(10) |
| O(9)–Sr(1)–O(8) | 80.10(10) | O(7)–Sr(1)–O(8) | 71.63(10) | O(5)–Sr(3)–O(8) | 94.10(10) | O(7)–Sr(3)–O(8) | 67.85(9) |
| O(2)–Sr(1)–O(1) | 69.83(11) | O(9)–Sr(1)–O(1) | 149.53(10) | O(6)–Sr(3)–O(4) | 110.56(10) | O(9)–Sr(3)–O(4) | 145.06(10) |
| O(7)–Sr(1)–O(1) | 75.31(10) | O(8)–Sr(1)–O(1) | 77.16(10) | O(5)–Sr(3)–O(4) | 99.06(10) | O(7)–Sr(3)–O(4) | 72.19(9) |
| O(2)–Sr(1)–C(81) | 76.15(12) | O(9)–Sr(1)–C(81) | 67.16(11) | O(8)–Sr(3)–O(4) | 77.13(9) | Sr(2)–O(1)–Sr(1) | 87.37(10) |
| O(7)–Sr(1)–C(81) | 145.53(11) | O(8)–Sr(1)–C(81) | 101.68(11) | C(2)–O(1)–Sr(2) | 140.8(3) | C(2)–O(1)–Sr(1) | 131.8(3) |
| O(1)–Sr(1)–C(81) | 137.46(11) | O(3)–Sr(2)–O(8) | 113.30(11) | C(4)–O(2)–Sr(1) | 139.9(3) | C(13)–O(3)–Sr(2) | 136.8(3) |
| O(3)–Sr(2)–O(7) | 146.76(11) | O(8)–Sr(2)–O(7) | 72.88(10) | C(15)–O(4)–Sr(2) | 129.3(3) | C(15)–O(4)–Sr(3) | 140.9(3) |
| O(3)–Sr(2)–O(1) | 134.60(11) | O(8)–Sr(2)–O(1) | 80.82(10) | Sr(2)–O(4)–Sr(3) | 89.51(10) | Si(1)–O(7)–Sr(2) | 118.95(14) |
| O(7)–Sr(2)–O(1) | 77.91(10) | O(3)–Sr(2)–O(4) | 72.38(11) | Si(1)–O(7)–Sr(1) | 125.0(2) | Sr(2)–O(7)–Sr(1) | 90.91(10) |
| O(8)–Sr(2)–O(4) | 82.15(10) | O(7)–Sr(2)–O(4) | 76.47(10) | Si(1)–O(7)–Sr(3) | 131.3(2) | Sr(2)–O(7)–Sr(3) | 91.35(10) |
| O(1)–Sr(2)–O(4) | 152.45(10) | O(3)–Sr(2)–C(45) | 88.02(13) | Sr(1)–O(7)–Sr(3) | 88.21(9) | Si(2)–O(8)–Sr(2) | 119.3(2) |
| O(8)–Sr(2)–C(45) | 139.89(12) | O(7)–Sr(2)–C(45) | 71.48(11) | Si(2)–O(8)–Sr(1) | 123.3(2) | Sr(2)–O(8)–Sr(1) | 90.06(10) |
| O(1)–Sr(2)–C(45) | 108.75(12) | O(4)–Sr(2)–C(45) | 72.20(12) | Si(2)–O(8)–Sr(3) | 133.8(2) | Sr(2)–O(8)–Sr(3) | 91.35(10) |
| O(6)–Sr(3)–O(9) | 99.76(11) | O(6)–Sr(3)–O(5) | 71.20(11) | Sr(1)–O(8)–Sr(3) | 87.10(9) | Si(3)–O(9)–Sr(1) | 121.2(2) |
| O(9)–Sr(3)–O(5) | 107.01(10) | O(6)–Sr(3)–O(7) | 127.34(10) | Si(3)–O(9)–Sr(3) | 144.4(2) | Sr(1)–O(9)–Sr(3) | 94.05(10) |

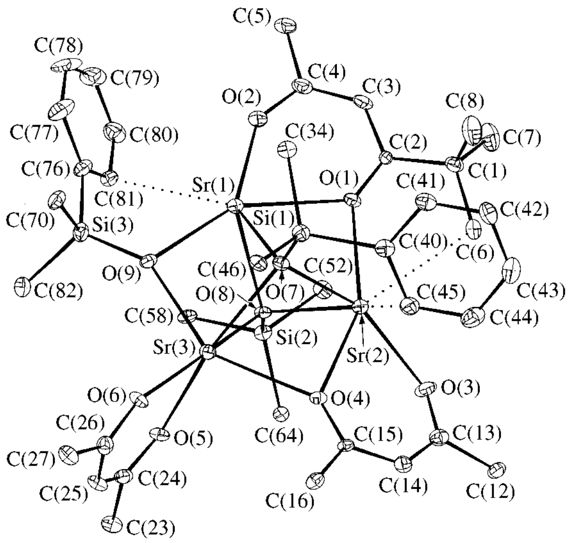

**Fig. 2** Molecular structure of $[Sr_3(tmhd)_3(OSiPh_3)_3]$ **3**. All solvent atoms, non-*ipso*-carbons except those having Sr···C interactions and hydrogen atoms are omitted for clarity

in the mass spectra. The observed molecular ions were from either decomposition fragments of the anionic ligands or from polymerised ligands based on O- and/or Si-containing backbones. Similar mass spectra have been observed previously for free polysiloxanes.[1,6] Additional molecular ions due to hmpa (*m*/*z* 179) and its various decomposition fragments were observed in the mass spectra for complexes **7** and **8**.[6] As the precise nature of complexes **3** and **9** could not be definitively elucidated by spectroscopic methods, single-crystal X-ray structural investigations were undertaken.

## Crystal structure of $[Sr_3(tmhd)_3(OSiPh_3)_3]$ 3

The molecular structure of $[Sr_3(tmhd)_3(OSiPh_3)_3]$ **3** is illustrated in Fig. 2, and selected bond lengths and angles given in Table 5. Complex **3** consists of triangular arrangement of Sr atoms with metal–metal non-bonded distances of Sr(1)···Sr(2) 3.544(2), Sr(2)···Sr(3) 3.654(2) and Sr(3)···Sr(1) 3.567(1) Å respectively. The molecule is stabilised by a combination of three tmhd and triphenylsiloxy ligands respectively. Two of the latter adopt $\mu_3$-bridging positions above and below the plane of metal atoms. A belt of oxygens [O(9), O(4) and O(1)] around the metal triangle is formed from the third siloxy ligand oxygen [O(9)] bridging across Sr(1) and Sr(3) and a bridging oxygen from each of the two tmhd ligands that are chelate/monoatomic bridging. The third tmhd acts in a conventional chelating manner to Sr(3) through O(5) and O(6).

The co-ordination numbers of both Sr(1) and Sr(2) are five, whilst Sr(3) is six-co-ordinate. The co-ordination geometry around Sr(3) can be viewed as severely distorted octahedral. The axial oxygen sites are taken by O(4) and O(9) and are both displaced from idealised octahedral geometries towards the centre of the metal triangle. The oxygens of the chelating tmhd ligand [O(5), O(6)] and the two $\mu_3$-bridging siloxy ligands [O(7), O(8)] are observed to occupy the remaining equatorial positions.

Atoms Sr(1) and Sr(2) have distorted trigonal-bipyramidal co-ordination environments with the equatorial oxygens of O(2), O(7), O(8) and O(3), O(7), O(8) respectively. Axial positions are occupied by O(1), O(9) and O(1), O(4) respectively. The bonding constraints of the $\mu$- and $\mu_3$-bridging oxygen sites appear to cause severe distortions from the idealised geometries. This is shown by the acuteness of the O(7)–Sr(1)–O(8) and O(7)–Sr(2)–O(8) angles [71.4(1) and 72.9(1)° respectively] and the displacement of the axial oxygens O(9) and O(1) [for Sr(1) and Sr(2) respectively] that bend in towards the centre of the metal triangle.

Careful analysis of interatomic distances shows that a phenyl carbon [C(81)] approaches Sr(1); this distance at 3.305(5) Å is considerably shorter than the appropriate sum of the van der Waals radii (3.70 Å) and may be considered to be a weak Sr···C interaction. Two comparable close contacts with the outer 'exposed face' of Sr(2) have been identified at 3.195(5) and 3.105(5) Å for the methyl (thmd) and phenyl (siloxy ligand) carbons C(6) and C(45) respectively. These values are again much less than the van der Waals radii sum although slightly longer than the average Sr–C bonding distance of 2.750(8) Å for the metal pentamethylcyclopentadienyl complex $[Sr(C_5Me_5)_2]$.[25] We therefore consider all these Sr–C ($\leqslant$3.31 Å) distances as weak bonding interactions. In fact, weak M···C interactions have also been suggested previously for the one-dimensional polymer $[Ba(C_5Me_5)_2]$,[25] in which the shortest Ba–C (methyl) distance is 0.28 Å longer than the shortest intramolecular Ba–C distance. With the inclusion of these contacts, the geometry around Sr(2) may be described as a monocapped octahedron with C(6) capping the triangular face formed by O(1), O(3) and C(45). Likewise, the additional interaction with C(81) gives a severely distorted octahedral co-ordination around Sr(1).

The Sr−O bonds to the three tmhd ligands in compound **3** lie in the range 2.347(3) to 2.646(3), and fall into three groups. The shortest of these distances [2.347(3) and 2.384(3), average 2.367 Å] involve the two terminal oxygen atoms [O(3) and O(2) respectively] from the two chelating/bridging tmhd ligands, whereas the bonds to the two bridging oxygens from the same ligands [O(1) and O(4)] are the longest [2.503(3) and 2.646(3), average 2.580 Å]. Although, the purely chelating tmhd ligand is generally expected to form the shortest bonds to the metal, such bonds from Sr(1) to O(5) and O(6) [2.441(3), 2.404(3) respectively, average 2.423 Å] are intermediate between the above two groups observed in the bridging ligands; this lengthening of the Sr−O bonds involving the purely chelating tmhd ligands may be attributed to the greater co-ordination number of Sr(3) compared with Sr(1) and Sr(2) (six *vs.* five). The Sr−O ($\mu$-diketonate) distances observed here are smaller than the corresponding bonds in the eight-co-ordinate $[Sr(tfpd)_4]^{2-}$ (tfpd = 1,1,1-trifluoropentane-2,4-dionate) dianion [2.530(2)–2.593(2), average 2.571 Å] in $[Htmen]_2[Sr(tfpd)_4]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine),[26] but are close to the corresponding values found in other related strontium β-diketonate complexes.[24,27]

The Sr−O bonds involving the three siloxy ligands also show large variations [2.436(3)–2.636(3) Å], and, as expected, those to the $\mu$-bridging ligands are shorter than those involving the two $\mu_3$-capping ligands. While the two bridging bonds [involving O(9)] are nearly symmetric [2.436(3), 2.440(3), average 2.438 Å], each of the $\mu_3$ ligands is bonded to the $Sr_3$ triangle quite asymmetrically, with two short and one long Sr−O bonds [2.447(3), 2.496(3) and 2.628(3), average 2.524 Å for O(7), and 2.469(3), 2.541(3) and 2.636(3), average 2.549 Å for O(8)]. The Sr−O (siloxy) distances observed in the present compound are slightly longer than those [2.429(4)–2.594(4), average 2.484 Å] involving the three $\mu$-bridging siloxy ligands in the dimer $[Sr_2(OSiPh_3)_4(NH_3)_5]\cdot 0.5C_6H_5Me$.[15] The average of all the Sr−O (siloxy) bonds (2.515 Å) is also marginally longer than the corresponding value for the tmhd ligands (2.487 Å).

Close examination of the parameters related to the structural core reveals that the $Sr_3(\mu\text{-}O)_3$ moiety shows significant deviations from planarity, with the bridging oxygens O(1), O(4) and O(9) being displaced from the $Sr_3$ plane by 0.079, 0.226 and 0.054 Å respectively. The two $\mu_3$-capping oxygens [O(7), O(8)] are placed nearly equidistant (1.456 and 1.481 Å respectively) on either side of this plane. The $\mu$-bridging atoms are virtually planar, with the sum of the interbond angles at O(1), O(4) and O(9) being 360.0, 359.7 and 359.6° respectively. The Sr−O−Sr angles involving the $\mu$-bridging as well as the $\mu_3$-capping oxygens all lie within a narrow band [87.10(9)–94.05(10)°] close to 90°, whilst the Sr−O−Si angles show large variations for the $\mu$-bridging [121.2(2)–144.2(2)°] and $\mu_3$-capping oxygens [118.95(14)–133.8(2)°]. The dimensions of the $OSiPh_3$ and tmhd ligands are as expected; it is observed, however, that in the β-diketonate ligands the two CO bonds are nearly equal for the purely chelating ligand, whereas there is *ca.* 0.03 Å difference in both the two chelating/bridging ligands, the longer value being associated with the $\mu$-bridging oxygens. The effect of the bridge formation is also reflected in the larger fold angles about the $O\cdots O$ axis for the bridging ligands compared with the purely chelating tmhd ligand [12.1(5) and 18.4(5) *vs.* 4.3(5)°].

The structure of complex **3** (Fig. 2) may be compared to that of the strontium β-diketonate complex $[Sr_3(tmhd)_6(Htmhd)]$,[24] which also has a triangle of strontium cations. The average $Sr\cdots Sr$ distance in complex **3** (3.588 Å) is much smaller than the corresponding distances in $[Sr_3(tmhd)_6(Htmhd)]$, in which the $Sr\cdots Sr$ distances are 3.631(5), 3.905(5) and 4.110(5) Å. This 'trimer' is stabilised by one $\mu_3$-oxygen and several $\mu$-oxygens all from tmhd ligands. This indicates the more compact nature of compound **3**, resulting from the presence of two $\mu_3$-oxygens from the two monodentate siloxy groups which cap opposite faces of the $Sr_3$ triangle. The $Sr_3O_9Si_3$ core is structurally very similar to the $Ba_3O_6Si_6$ core of $[Ba_3(OSiPh_3)_6(thf)]\cdot 0.5thf$ (thf = tetrahydrofuran).[5] The latter complex consists of a triangle of cations capped by two $\mu_3$-bridging siloxy ligands and a belt of three bridging oxygens around the triangle, in this case provided exclusively by $\mu$-bridging siloxy ligands. Atoms Ba(1) and Ba(3) are additionally co-ordinated to a terminal triphenylsiloxy ligand and a thf molecule respectively, to obtain molecular neutrality and effectively satisfy the co-ordination requirements of the metals. As in complex **5**, the M−O (siloxy) bonding distances in $[Ba_3(OSiPh_3)_6(thf)]\cdot 0.5thf$ follow the expected pattern, increasing in the order terminal, $\mu$-bridging, and $\mu_3$-bridging.

### Crystal structure of $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ 9

An X-ray study of $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ **9** showed that this compound is structurally very similar to the barium complexes $[Ba_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot 0.5C_6H_5Me$ **10**[18] and $[Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)]$ **8**,[18] all of which contain an array of three metal atoms held together by six $\mu$-bridging oxygens from three tetraphenyldisiloxydiolate dianions. In all cases the arrangements of the three metal atoms are nearly linear with angles at the central atom being very similar, 174.16(5), 172.6(1) and 167.0(1)° for **9**, **10** and **8** respectively. The general view of the structure of **9** is shown in Fig. 3, whilst its $Sr_3(OSiOSiO)_3$ central core is illustrated in Fig. 4. Selected bond lengths and angles are given in Table 6. Although the unique polyether molecule terminally bound to Sr(2) was extensively disordered (only fourteen out of its fifteen non-hydrogen atoms located and isotropically refined with bond-length constraints), the true identity of the material (complex **9**) and basic geometry of the $Sr_3(OSiPh_2OSiPh_2O)_3$ framework were established beyond doubt.

The central strontium atom lies on a two-fold axis and is six-co-ordinated with a distorted trigonal-prismatic geometry, whilst the other two terminal strontium atoms (related by two-fold axis) are seven-co-ordinated, each involving the three bridging oxygen atoms and four oxygens from the tetraglyme molecule making an 'umbrella' arrangement from the end. The Sr−O distances involving the tetraphenyldisiloxydiolate ligands range from 2.414(6) to 2.608(6) Å and the average value 2.493 Å is comparable with that (2.484 Å) found for the $\mu$-bridging Sr−O (Si) distance in $[Sr_2(OSiPh_3)_4(NH_3)_5]\cdot 0.5C_6H_5Me$,[15] but somewhat longer than the average (2.438 Å) in $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot 0.5C_6H_5Me$. All three $O{-}SiPh_2{-}O{-}SiPh_2{-}O$ strands bend away from the central cation with Si−O−Si angles of 145.2(4) (twice) and 163.5(7)°. The more obtuse angle of the third tetraphenyldisiloxydiolate chain is accompanied by the longest Sr−O (Si) distances to the central cation [Sr(1)−O(11), Sr(1)−O(11′) 2.608(6) Å] and the shortest bonds to the terminal cations [Sr(2)−O(11), Sr(2)−O(11′) 2.414(6) Å]. The Sr(1)−O(12), Sr(2)−O(12′), Sr(1)−O(13), Sr(2)−O(13) distances [2.525(6), 2.459(7), 2.537(6) and 2.414(6) Å respectively] reveal that these Sr−O−Sr bridges are also asymmetric. The O−Sr−O angles in each unique half of the $SrO_3SrO_3Sr$ core are all acute and lie in the range 73.0(2)–75.3(2)°, whilst the Sr−O−Sr bridge angles are closer to 90° having values in the narrow range 87.5(2)–89.1(2)°.

The two compounds **9** and **10**[18] have a nearly isostructural relationship as suggested by very similar unit-cell dimensions and the same space group. Upon closer examination, however, some subtle differences are observed which can be attributed to the differences in cationic radii, 1.32 and 1.49 Å for $Sr^{2+}$ and $Ba^{2+}$ (co-ordination number 6 assumed for both) respectively.[28]

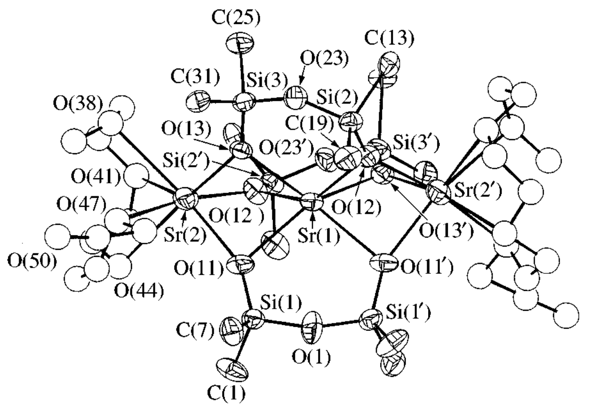

**Fig. 3** Molecular structure of $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]$ **9**, showing the atom numbering scheme. All solvent atoms, hydrogen atoms and non-*ipso*-C atoms have been omitted for clarity

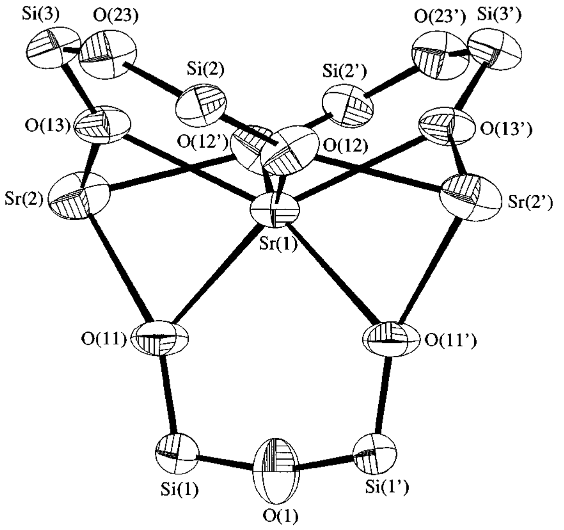

**Fig. 4** Structure of the $Sr_3(OSiOSiO)_3$ central core of $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]$ **9**, showing the symmetry-related atoms

**Table 6** Selected bond lengths (Å) and angles (°) for $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ **9**

| | | | |
|---|---|---|---|
| Sr(1)–O(12) | 2.525(6) | Sr(1)–O(13) | 2.537(6) |
| Sr(1)–O(11) | 2.608(6) | Sr(2)–O(11) | 2.414(6) |
| Sr(2)–O(13) | 2.414(6) | Sr(2)–O(12′) | 2.459(7) |
| Sr(2)–O(47) | 2.61(2) | Sr(2)–O(44) | 2.712(14) |
| Sr(2)–O(41) | 2.728(11) | Sr(2)–O(38) | 2.860(14) |
| Sr(2′)–Sr(1)–Sr(2) | 174.16(5) | O(12)–Sr(1)–O(12′) | 143.6(3) |
| O(12)–Sr(1)–O(13′) | 75.3(2) | O(12)–Sr(1)–O(13) | 88.7(2) |
| O(13′)–Sr(1)–O(13) | 127.7(3) | O(12)–Sr(1)–O(11′) | 73.0(2) |
| O(13)–Sr(1)–O(11′) | 146.8(2) | O(12)–Sr(1)–O(11) | 134.6(2) |
| O(13)–Sr(1)–O(11) | 75.0(2) | O(11′)–Sr(1)–O(11) | 98.1(2) |
| O(11)–Sr(2)–O(13) | 80.9(2) | O(11)–Sr(2)–O(12′) | 77.6(2) |
| O(13)–Sr(2)–O(12′) | 78.8(2) | O(11)–Sr(2)–O(47) | 93.0(4) |
| O(13)–Sr(2)–O(47) | 101.5(4) | O(12′)–Sr(2)–O(47) | 170.5(4) |
| O(11)–Sr(2)–O(44) | 91.7(4) | O(13)–Sr(2)–O(44) | 166.3(3) |
| O(12′)–Sr(2)–O(44) | 111.0(3) | O(47)–Sr(2)–O(44) | 67.2(4) |
| O(11)–Sr(2)–O(41) | 136.6(3) | O(13)–Sr(2)–O(41) | 130.2(3) |
| O(12′)–Sr(2)–O(41) | 80.2(3) | O(47)–Sr(2)–O(41) | 106.2(4) |
| O(44)–Sr(2)–O(41) | 62.5(4) | O(11)–Sr(2)–O(38) | 161.0(3) |
| O(13)–Sr(2)–O(38) | 92.6(3) | O(12′)–Sr(2)–O(38) | 118.8(3) |
| O(47)–Sr(2)–O(38) | 70.7(4) | O(44)–Sr(2)–O(38) | 90.8(4) |
| O(41)–Sr(2)–O(38) | 60.2(4) | Sr(2)–O(11)–Sr(1) | 87.5(2) |
| Sr(2′)–O(12)–Sr(1) | 88.4(2) | Sr(2)–O(13)–Sr(1) | 89.1(2) |
| Si(1′)–O(1)–Si(1) | 163.5(7) | Si(1)–O(11)–Sr(2) | 155.3(4) |
| Si(1)–O(11)–Sr(1) | 117.2(3) | Si(2)–O(12)–Sr(2′) | 145.6(4) |
| Si(2)–O(12)–Sr(1) | 125.9(4) | Si(3)–O(13)–Sr(2) | 143.6(4) |
| Si(3)–O(13)–Sr(1) | 126.9(3) | Si(3)–O(23)–Si(2) | 145.2(4) |

The primed atoms in this table and in Figs. 3 and 4 belong to one and the same molecule and are generated by the symmetry operation $1 - x, -y, z$.

First in complex **10** one of the oxygen atoms belonging to the Si–O–Si moieties approaches the central barium atom to within bonding distance [Ba(1)–O(1) 3.14(1) Å], whilst in **9** the same atom is pushed outside the co-ordination sphere [Sr(1) ··· O(1) 3.469 Å] causing a reduction in co-ordination number of the central atom. Secondly in **10** all the five oxygen atoms of the tetraglyme molecule approach the terminal barium within bonding distances [Ba–O (tetraglyme) 2.882–3.257 Å], whereas in **9** only four oxygen atoms of this ligand are bonded to the terminal strontium [Sr–O (tetraglyme) 2.61(2)–2.86(1) Å] and the fifth oxygen (one terminal OMe group) lies far outside the co-ordination sphere. Although the Sr–O (tetraglyme) distances have relatively large estimated standard deviations (e.s.ds), the exact nature of the binding of tetraglyme to strontium is clearly established. Compared with the stoichiometrically equivalent barium compound **10**, the smaller cationic size of strontium is responsible for the reduction in co-ordination number of not only the central metal, but also of the terminal metals. Finally, as expected, the smaller $Sr^{2+}$ cations (compared to $Ba^{2+}$) are able to come closer together [Sr ··· Sr 3.4758(12) Å] effectively causing a 'compression' of the core compared with complex **10** [Ba ··· Ba 3.766(1) Å] and **8** [Ba ··· Ba 3.781(5), 3.809(5) Å].[18] This effect is reflected in the narrower Si–O–Si angles at O(1) and O(23) [163.5(7) and 145.2(4)°] for **9** compared with those [174.7(10) and 151.3(9)°] in **10**. However, the corresponding values in **8** [164.3(14), 152.0(15) and 146.2(14)°] are comparable with those found in the present compound. The large Si–O–Si angles observed in the above heavily strained six-membered metallosiloxane ring systems can be contrasted with the angles 120–131° for relatively strain-free silyl ethers,[29] but comparable with those (*ca.* 160°) for the larger eight-membered ring system in $Ph_4Si_4O_4$.[30] The exclusive inward bending of the silyl ether oxygen from one tetraphenyldisiloxydiolate chain towards the central barium cation in both compounds **8** and **10** suggests a highly strained six-membered ring system. This is, however, compensated by the additional stabilisation energy resulting from the increase in co-ordination number of the central barium cation. In compound **9** the binding of Sr(1) to any of the central silyl ether oxygens [*e.g.* O(1)] is excluded on steric grounds resulting from relatively shorter metal–metal (Sr ··· Sr) distances. It is probable that any additional stabilisation gained from the increase in co-ordination number of the central strontium (*via* a dative bond from one of the silyl ether oxygens) would be unable to compensate for the expected increase in intramolecular ring strain.

## Conclusion

The syntheses of bis(*tert*-butyldimethylsiloxy)-complexes of Sr and Ba *via* the ammoniacal hydrocarbon solvent route have been successful. Likewise, silanolysis of $[\{Sr(OEt)_2(HOEt)_4\}_n]$[19] with an excess of $HOSiMe_2Bu^t$ gave the corresponding insoluble siloxy-complex $[Sr(OSiMe_2Bu^t)_2]_n$. This suggests that the $Me_2Bu^t$ substituents on Si are sufficiently small to promote extensive bridging, leading to polymeric compounds. The metal co-ordination spheres in these compounds are thus satisfied and show little tendency to bind additional Lewis base(s). Although complexes **1** and **2** could not be structurally characterised by diffraction methods due to the lack of suitable single crystals, the spectroscopic data confirmed their purity and provided some evidence regarding their structures. In particular, the $^{29}Si-\{^1H\}$ NMR solution spectra for **1** and **2** in co-ordinating solvents [*e.g.* $(CD_3)_2SO$] suggested that both bridging and terminal environments existed in such solvents. Terminal siloxy ligands have been reported to resonate generally at higher fields (lower ppm) with respect to bridging ligands.[15,23,31] Therefore, deaggregation to discrete monomers was unlikely in these cases, although a mixture of products cannot be discounted.

The condensation reaction of $Ph_2Si(OH)_2$ in ammoniacal toluene mixtures of these metals has provided a high-yield route to the respective complexes. The complete elimination of ammonia and water from complexes **5** and **6** to form the respective $[M_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ (M = Sr **9** or Ba **10**) complexes was largely attributed to the chelating effect associated with the ligand.

A possible explanation for the adoption of a trimer, rather than a smaller ensemble for $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$ **3**, may have been due to the absence of a suitable Lewis base (such as ammonia or tetraglyme) in the reaction mixture which could occupy accessible co-ordination sites {*cf.* the 'dimers' $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot0.5C_6H_5Me$ and $[Sr_2(OSiPh_3)_4(NH_3)_5]\cdot0.5C_6H_5Me$ and the monomers $[M(OSiPh_3)_2(tetraglyme)]$ (M = Ca or Sr)}.[14,15] Therefore, two triphenylsiloxy ligands are required to triply (rather than doubly) bridge in order to satisfy the co-ordination requirements of the metals. The arrangement of two $\mu_3$-bridging triphenylsiloxy ligands above and below the plane of cations may have been adopted because it also maximises ligand co-ordination numbers without greatly increasing intramolecular repulsions. Comparing the amount of tmhd in compound **3** with that in the complex $[Sr_3(tmhd)_6(Htmhd)]$ suggests that the triphenylsiloxy ligands are highly effective at shielding the molecule despite being monodentate compared to the tmhd ligands which are bidentate. As a result the average metal co-ordination number for compound **3** was smaller than that in $[Sr_3(tmhd)_6(Htmhd)]$ without affecting the degree of oligomerisation. Additionally, the triphenylsiloxy ligands in compound **3** appear to prefer bridging, as opposed to terminal, bonding modes. One explanation for this is that these ligands do not have two competing oxygens sites (as in tmhd), therefore they are more free to bind at bridging sites. This could explain why μ-bridging Sr−O bond lengths for the triphenylsiloxy ligands are shorter than in the related strained tetraphenyldisiloxydiolate systems.[6,15]

X-Ray crystallographic studies have shown that the metallotetraphenyldisiloxydiolate cores for barium and strontium are related and each contains three cations stabilised by an equal number of tetraphenyldisiloxydiolate ligands. This structural preference appears to be somewhat motivated by the need to optimise cation co-ordination numbers, with minimum intramolecular repulsion and ring strain. Thus, for a range of strongly co-ordinating Lewis-base-adducted complexes, the respective central cores remained intact, with only the co-ordination geometries of the outer cations being affected. The solid-state $^{29}Si-\{^1H\}$ NMR spectrum for $[Sr_3\{O(SiPh_2O)_2\}_3(hmpa)_5]\cdot C_6H_5Me$ **7** suggesting differing silicon environments was consistent with a proposed trimeric structure, in which the tetraphenyldisiloxydiolate ligands are slightly unequal (due to five asymmetrically co-ordinated hmpa ligands in the trimer).

The rigid geometrical constraints imposed upon the respective ligands in $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$ **3** resulted in at least two strontium atoms with partial hemispheres that were sterically accessible to Lewis bases. Consequently, the binding of weak donors of this type effectively increased the co-ordination number of two strontium cations with little (if any) change in intramolecular repulsive energies. It is believed that the distortion from idealised co-ordination geometries of the cations may have been due to the (hard) ligand constraints in 'cementing' together the triangle and not primarily because of the weak Sr···C contacts that filled the remaining metal co-ordination sites. The presence of such weak interactions in compound **3** is desirable because they represent possible sites for nucleophilic attack, which could be exploited to synthesize mixed-metal compounds. Furthermore, the use of mixed-ligand compounds could be useful for fine tuning the precursors to achieve desired characteristics and properties.

## Experimental

### General procedures and instrumentation

All manipulations were carried out under an atmosphere of dry (molecular sieves) argon using standard dry-box and Schlenk-like techniques. Elemental analyses were performed by the Microanalytical Department of Imperial College. Melting points were measured under argon in sealed capillaries using an Electrothermal apparatus and are uncorrected. Samples for solubility tests were prepared in an inert atmosphere of argon and conducted in rubber-topped vials.

Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer as either Nujol or hexachlorobutadiene (hcb) mulls between 25 × 4 mm CsI plates. The Nujol and hcb were both predried with 4 Å molecular sieves prior to use (and stored in the glove-box); the samples were protected from the atmosphere by an O-ring-sealed Presslok™ holder (Aldrich). All NMR solution samples were prepared in the glove-box, using 5 mm NMR tubes fitted with Young's valves. Solution NMR spectra were recorded on a JEOL GS 270 MHz spectrometer; $^1H$ spectra were recorded for 16 scans at 270.16 MHz, whilst $^{13}C-\{^1H\}$ solution spectra were obtained at 67.94 MHz. Chemical shifts were referenced to tetramethylsilane (*ca.* 1%) added by volume or using the protio impurities of the deuteriated solvent. The $^{29}Si-\{^1H\}$ NMR solution spectra were referenced against $SiMe_4$ and recorded at 53.67 MHz, using the NNE (gated) pulse sequence (shift range ±90 ppm) with a pulse delay of 8 s, whilst $^{31}P-\{^1H\}$ NMR solution spectra were referenced against phosphoric acid (85% solution in water) and recorded at 109.37 MHz; solid-state $^{29}Si-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker instrument at University College, London University Solid State NMR service using the CP MAS (cross polarisation magic angle spinning) and MAS/DEC (magic angle spinning/proton decoupled) modes respectively. Controlled thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements on the complexes were done using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by an Omni Pro 486DX-33 personal computer. The mass of the samples investigated was between 19 and 27 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 $cm^3\ min^{-1}$) nitrogen gas, using heating rates of 15 °C $min^{-1}$.

### Starting materials

All hydrocarbon solvents were rigorously predried and then distilled over the appropriate drying agents. The NMR solvents, tetraglyme, hmpa (Aldrich chemicals) and Htmhd (Inorgtech Chemicals) were all dried over 4 Å molecular sieves prior to use and stored under argon in glass containers fitted with greaseless Young's valves. The compounds $[\{Sr(OEt)_2(HOEt)_4\}_n]$ and $HOSiMe_2Bu^t$ were prepared according to literature methods.[6,19,32] Triphenylsilanol, diphenylsilanediol (Aldrich), and strontium (Aldrich) and barium (Aldrich) granules were stored in an inert-atmosphere glove-box. The ammonia gas cylinder was obtained from BOC. **CAUTION:** care should be taken when using ammonia gas and working with ammoniacal metal mixtures by performing all ammoniation reactions in well ventilated fume cupboards. Also, hmpa is extremely toxic.

### Preparations

**$[Sr(OSiMe_2Bu^t)_2]_n$ 1.** *Method A.* Strontium metal granules (0.88 g, 10.0 mmol), preweighed in a glove-box, were placed in a large Schlenk tube along with *tert*-butyldimethylsilanol (2.64 g, 20.0 mmol) and toluene (25.0 $cm^3$). The reaction mixture was cooled to −40 °C and $NH_3$ gas was carefully bubbled through the reaction mixture for 0.5 h (when all the metal had dissolved). The mixture was allowed to reach room temperature slowly to give a clear solution, which on gentle heating from a heat-gun gave a white suspension. All the solvent was removed *in vacuo*, giving a soft white solid with a camphorous odour. Strong heating was avoided, as large amounts of product tended to sublime if due care was not taken (2.83 g, 81%), m.p. >297 °C (Found: C, 40.2; H, 8.3. $C_{12}H_{30}O_2Si_2Sr$ requires C, 41.6; H, 8.5%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1358m, 1253m, 1005w, 926s, 829s, 813m, 762s and 659m; (hcb) 2948s, 2925vs, 2881m, 2851vs, 1469m, 1404m, 1385m, 1357m, 1253vs, 1211vw, 1004m, 828vs, 811s, 762vs, 574vw and 414s; $\delta_H[(CD_3)_2SO]$ 0.81 ($CCH_3$) and −0.17 (s, $SiCH_3$); $\delta_{C(H)}[(CD_3)_2SO]$ 28.2 (s, br, $CCH_3$), 19.8 ($CCH_3$) and 0.2 (s, br, $SiCH_3$).

*Method B.* Strontium ethoxide crystals $[\{Sr(OEt)_2(HOEt)_4\}_n]$ (3.62 g, 10.0 mmol), preweighed in a glove-box, were placed in a Schlenk tube along with *tert*-butyldimethylsilanol (2.64 g, 20 mmol) and toluene (20.0 cm$^3$). The reaction mixture was refluxed for 1.5 h after which time the solvent was removed *in vacuo* to give a soft white solid (2.51 g, 72%). Spectroscopic and analytical data are identical to those obtained by method A.

**$[Ba(OSiMe_2Bu^t)_2]_n$ 2.** The reaction was performed using identical conditions and molar ratios to those employed in the synthesis of compound **1** (method A), but with barium metal granules (1.37 g, 10.0 mmol) rather than calcium. Strong heating was avoided as large amounts of product tended to sublime if due care was not taken. The product was obtained as a soft white powder upon removal of all solvent *in vacuo* (3.00 g, 75%), m.p. >290 °C (Found: C, 35.6; H, 6.9. $C_{12}H_{30}BaO_2Si_2$ requires C, 36.1; H, 7.5%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2922vs, 1252s, 1019m, 929vs, 825vs, 810s, 750vs and 654w; (hcb) 2925vs, 2880m, 2850vs, 1468m, 1403w, 1384m, 1350m, 1248s, 937vs, 825vs, 758vs and 411m; $\delta_H[(CD_3)_2SO]$ 0.81 ($CCH_3$) and −0.16 ($SiCH_3$); $\delta_{C(H)}[(CD_3)_2SO]$ 28.0 ($CCH_3$), 19.4 ($CCH_3$) and 0.0 ($SiCH_3$).

**$[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot 0.5C_6H_5Me$ 3.** Strontium ethoxide crystals $[\{Sr(OEt)_2(HOEt)_4\}_n]$ (3.98 g, 11.0 mmol), preweighed in a glove-box, were placed in a Schlenk tube along with toluene (25.0 cm$^3$). The mixture was refluxed at 100 °C for 10 min, after which time triphenylsilanol (3.04 g, 11.0 mmol) and Htmhd (2.3 cm$^3$, 11.0 mmol) were added. All volatiles were removed *in vacuo* and the product was redissolved in hot toluene (10.0 cm$^3$). Colourless blocks were obtained after the solution was allowed to stand at room temperature for 3 h (4.21 g, 70%), m.p. 195–198 °C (Found: C, 64.1; H, 6.1. $C_{90.5}H_{106}O_9Si_3Sr_3$ requires C, 64.5; H, 6.3%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2961m, 2926m, 1590m, 1505m, 1495m, 1455m, 1428s, 1110s, 1028m, 729m, 712s, 698s and 515m; $\delta_H[(CD_3)_2SO]$ 7.60 (s, br, *o*-H of Ph), 7.20 (m, vbr, *m*-, *p*-H of Ph and $C_6H_5Me$), 5.80 (s, tmhd CH), 2.20 (s, $C_6H_5CH_3$) and 1.20 (s, tmhd $CH_3$); $\delta_{C(H)}[(CD_3)_2SO]$ 201.0 (tmhd CO), 145.0 (*ipso*-C of Ph), 136.4 (*o*-C of Ph), 127.6 (*m*-C of Ph), 127.4 (*p*-C of Ph), 90.9 (tmhd CH), 41.0 (tmhd $CCH_3$) and 28.2 (s, tmhd $CH_3$).

**$[\{Ca[O(SiPh_2O)_2](H_2O)_{0.3}(NH_3)_{0.3}\}_n]$ 4.** Calcium metal granules (0.40 g, 10.0 mmol), preweighed in a glove-box, were placed in a large Schlenk tube along with diphenylsilanediol (4.32 g, 20.0 mmol) and toluene (25.0 cm$^3$). The reaction mixture was cooled to −40 °C and ammonia gas was bubbled in with stirring of the mixture for 35 min, giving a dark grey suspension. When left to warm up over an hour the mixture gave a white suspension which did not solubilise upon strong heating. The solvent was removed under reduced pressure to give a dry white solid (4.20 g, 88%), m.p. >210 °C (Found: C, 61.3; H, 4.8; N, 0.5. $C_{24}H_{22.4}CaN_{0.3}O_4Si_2$ requires C, 60.6; H, 4.8; N, 0.6%); $\tilde{\nu}_{max}/cm^{-1}$ (hcb) 3646w, 3484vw, 3372vw, 3300w (br), 3295vw, 3132vw, 3064w, 3049w, 2998w, 1589w, 1428m, 1261vw, 1117s, 1045s, 1032s, 1015s, 742m, 704s, 682vw, 525s and 487m; compound did not sublime at $0.5 \times 10^{-4}$ Torr (190 °C); $\tilde{\nu}_{max}/cm^{-1}$ for sublimation residue (Nujol) 2925m, 1430m, 1119s, 1027m, 1020m, 800m, 745m, 699m and 526s.

**$[\{Sr[O(SiPh_2O)_2](H_2O)(NH_3)\}_n]$ 5.** The reaction was set up using identical conditions and molar ratios as for compound **4**, but strontium metal turnings (0.88 g, 10.0 mmol) rather than calcium were used. Ammonia gas was bubbled in for 25 min giving a dark grey suspension. When left for 1 h to warm up the suspension became colourless. External heating by a heat-gun and removal of the solvent under reduced pressure gave a white solid (4.95 g, 93%), m.p. >245 °C (Found: C, 54.4; H, 4.3; N, 2.6. $C_{24}H_{25}NO_4Si_2Sr$ requires C, 53.8; H, 4.7; N, 2.6%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3620vw, 3380vw, 3300w (br), 1589m, 1428m, 1304vw, 1262w, 1117s, 993s, 802w, 741m, 700s, 630w, 614w, 530s, 494m and 418m; (hcb) 3621vw, 3383vw (broad base), 3200w, 3067m, 3047m, 2989m, 2925w, 1958vw, 1590m, 1428m, 1261m, 1110s, 742m, 701s, 683m, 629vw, 615vw, 532s, 516m and 418w; compound did not sublime at $10^{-4}$ Torr/210 °C; $\tilde{\nu}_{max}/cm^{-1}$ for sublimation residue (Nujol) 2957m, 2924s, 2853s, 1463m, 1428w, 1377w, 1261m, 1020m, 800m, 740w, 699m and 526m.

**$[\{Ba[O(SiPh_2O)_2](H_2O)(NH_3)_{0.3}\}_n]$ 6.** This compound has been briefly reported previously.[6,18] Additional data: m.p. >295 °C; $\tilde{\nu}_{max}/cm^{-1}$ (hcb) 3627w, 3545vw, 3380w (sharp peak, broad base), 3130w, 3065m, 3045m, 3022m, 2995m, 2920w, 1587m, 1495m, 1482w, 1428m, 1261w, 1184m, 1119s, 1051s, 741m, 729m, 705s, 682m, 624w and 612w: compound did not sublime at $0.25 \times 10^{-4}$ Torr/200 °C; $\tilde{\nu}_{max}/cm^{-1}$ for sublimation residue (hcb) 3049w, 2998w, 1590w, 1427m, 1118s, 1035vs, 1015s, 742m, 704s and 524s.

**$[Sr_3\{O(SiPh_2O)_2\}_3(hmpa)_5]\cdot C_6H_5Me$ 7.** *Method A.* The reaction was set up using identical conditions and molar ratios to those employed in the synthesis of compound **2**, but additionally in the presence of hmpa (5.25 cm$^3$, 30.0 mmol) and bubbling of $NH_3$ for only 25 min at −40 °C. When left to warm up over 1 h the mixture gave a white suspension. Application of external heat from a heat-gun gave a near colourless solution. The solution was layered with *n*-hexane (20.0 cm$^3$) and over 12 h yielded large crystalline blocks (5.30 g, 64%), m.p. 177–189 °C (Found: C, 51.7; H, 5.8; N, 7.9. $C_{109}H_{158}N_{15}O_{14}P_5Si_6Sr_3$ requires C, 52.6; H, 6.4; N, 8.4%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3040w, 2924s, 1426s, 1300s, 1197s, 1111s, 1033s, 1013s, 987s, 742s, 703s, 681w and 528w; (hcb) 3131w, 3063m, 3043m , 2994m, 2922s, 2804m, 1587m, 1484m, 1455s, 1426s, 1299s, 1197s, 1111s, 1033s, 742s, 702s, 681m, 528s and 500m; $\delta_{P(H)}(C_6D_6)$ 24.17; $\delta_{P(H)}[(CD_3)_2SO]$ 25.32; $\delta_{P(H)}$(solid state, MAS/DEC) 23.40.

*Method B.* Compound **5** (2.00 g, 3.7 mmol) was refluxed in a toluene suspension at 110 °C for 2 h, during which time hmpa (1.9 cm$^3$, 11.1 mmol) was slowly added. The solvent was removed under reduced pressure to give an oil that was heated for 1 h at 110 °C. Toluene (25.0 cm$^3$) was added during heating to yield a near colourless solution. The solution was slowly layered with an equivalent volume of *n*-hexane to obtain large colourless blocks (2.64 g, 86%). Spectroscopic and analytical data were identical to those from method A.

**$[Ba_3\{O(SiPh_2O)_2\}_3(hmpa)_5(H_2O)]$ 8.** The synthesis and spectroscopic characterisation for this compound have been reported previously.[6,18] This complex was also synthesized from the reaction of barium metal with 2 molar equivalents of diphenylsilanediol and hmpa respectively, in ammoniacal toluene solution at −40 °C. It was obtained in near-quantitative yield from a hot toluene solution which was left to cool to room temperature and then layered with *n*-hexane. Additional data: melts slowly >174 °C; $\tilde{\nu}_{max}/cm^{-1}$ (hcb) 3624vw, 3171vw (br), 3132w, 3082m, 3063s, 3043s, 2994s, 2886s, 2803s, 1952vw, 1884vw, 1587m, 1485s, 1463s, 1426s, 1379m, 1298s, 1171m, 1111s, 1012s, 983m, 894m, 743s, 700s, 681m, 625m and 612m; $\delta_{P(H)}(C_6D_6)$ 24.54 (s); $\delta_{P(H)}$(solid state, MAS/DEC) 24.73, 23.36 and 22.74.

**Table 7** Crystal data and details of data collection and refinement for $[Sr_3(tmhd)_3(OSiPh_3)_3]\cdot0.5C_6H_5Me$ **3** and $[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ **9**

| | Complex **3** | Complex **9** |
|---|---|---|
| Formula | $C_{87}H_{102}O_9Si_3Sr_3\cdot$<br>$0.5C_6H_5Me$ | $C_{92}H_{104}O_{19}Si_6Sr_3\cdot$<br>$0.5C_6H_5Me$ |
| *M* | 1684.88 | 1991.22 |
| Crystal system | Triclinic | Tetragonal |
| *a*/Å | 13.617(5) | 17.813(4) |
| *b*/Å | 13.824(5) | 17.813(4) |
| *c*/Å | 25.472(6) | 30.064(8) |
| α/° | 96.66(3) | |
| β/° | 93.06(3) | |
| γ/° | 115.10(2) | |
| $U$/Å$^3$ | 4 285(3) | 9539(4) |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{4}c2$ (no. 116) |
| $D_c$/g cm$^{-3}$ | 1.306 | 1.386 |
| *F*(000) | 1754 | 4124 |
| μ(Mo-Kα)/cm$^{-1}$ | 19.57 | 17.94 |
| Crystal size/mm | 0.35 × 0.22 × 0.15 | 0.35 × 0.25 × 0.20 |
| θ Range for data/° | 1.76–25.09 | 1.75–24.91 |
| $h_{min}$, $h_{max}$ | −16, 12 | −20, 11 |
| $k_{min}$, $k_{max}$ | −15, 15 | −19, 19 |
| $l_{min}$, $l_{max}$ | −28, 29 | −33, 33 |
| Total data measured | 17 898 | 37 765 |
| Total unique | 11 865 | 7619 |
| $R_{int}$ | 0.0515 | 0.0838 |
| Total observed | 7957 | 3693 |
| No. parameters | 973 | 449 |
| $\rho_{min}$, $\rho_{max}$/e Å$^{-3}$ | −0.41, +1.457 | −0.48, +0.78 |
| Absolute structure parameter | — | −0.009(13) |
| *R* [a] | 0.0639 (0.0410) [b] | 0.1129 (0.0642) [b] |
| *wR* [a] | 0.0968 (0.0934) [b] | 0.1760 (0.1622) [b] |

[a] $R = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = [\max(F_o^2) + 2(F_c^2)]/3$ with $a = 0.0394$ for complex **3** and 0.0880 for **9**. [b] The *R* value calculated for observed data $[F_o > 4\sigma(F_o)]$ only is given in parentheses.

**$[Sr_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ 9.** *Method A.* The reaction was set up using identical conditions and molar ratios to those employed in method A for the synthesis of compound **7**, but additionally in the presence of tetraglyme (2.2 cm$^3$, 10.0 mmol) rather than hmpa. The mixture was ammoniated for 20 min at −40 °C and then left to warm up over 1 h. This resulted in a turbid solution, which, when refluxed *via* an oil-bath for 1 h, gave a near colourless solution. The product crystallised as oblong blocks over 24 h at room temperature (4.40 g, 68%), m.p. >170 °C (Found: C, 47.7; H, 4.4. $C_{95.5}H_{108}O_{19}Si_6Sr_3$ requires C, 48.1; H, 4.4%); $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol) 2726vw, 1586vw, 1427m, 1299w, 1261w, 1201vw, 1183vw, 1112m, 1074m, 1031s, 1010s, 860m, 802m, 739m, 700m, 519m and 484m; (hcb) 3130vw, 3063m, 3043m, 2995m, 2927m, 2878m, 1957vw, 1587m, 1479m, 1455m, 1427m, 1364m, 1349w, 1298m, 1261m, 1200m, 1112s, 1073s, 1032s, 1010s, 740m, 702s, 600m, 619vw, 520s and 425m.

*Method B.* The reaction was performed using identical conditions and molar ratios to those employed in method B for the synthesis of compound **7**; however, tetraglyme (0.8 cm$^3$, 3.7 mmol) rather than hmpa was slowly added to give a solution. Colourless blocks were obtained by leaving the hot toluene solution to stand at room temperature (2.07 g, 87%). Spectroscopic and analytical data were identical to those from method A.

**$[Ba_3\{O(SiPh_2O)_2\}_3(tetraglyme)_2]\cdot0.5C_6H_5Me$ 10.** The synthesis and spectroscopic and structural characterisation for this compound were briefly reported previously.[6,18] This complex was also synthesized, in near-quantitative yield, from the reaction of barium metal with 2 molar equivalents of diphenylsilanediol and tetraglyme respectively, in ammoniacal toluene solution at −40 °C. Colourless crystals were obtained from a hot toluene solution left to cool to room temperature over a few hours. Additional data: decomposes >278 °C; $\tilde{\nu}_{max}$/cm$^{-1}$ (hcb) 3082w, 3062s, 3043s, 3005m, 2994m, 2923s, 2876s, 1587m, 1495w, 1476m, 1455m, 1427s, 1353w, 1298m, 1253m, 1200m, 1111s, 1049s, 894w, 793s, 741m, 700s, 680m and 655s.

### X-Ray crystallography

Suitable crystals of complexes **3** and **9** were obtained as described above, and mounted using silicon oil and transferred to the goniostat. All crystallographic measurements were made at 150 K using a Delft Instruments FAST TV area-detector diffractometer positioned at the window of a rotating-anode generator using Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[14] The data were corrected for Lorentz-polarisation factors and, for **3** only, also for absorption[33] (minimum and maximum absorption correction factors 0.897, 1.013). Absorption effects were ignored for complex **9**.

The structures were solved by direct methods (SHELXS 86)[34] and difference syntheses, and refined on $F^2$ by full-matrix least squares (SHELXL 93)[35] using all unique data. The non-hydrogen atoms for complex **3** were all anisotropic; the toluene molecule (solvate) was disordered about the centre of symmetry (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) with the three unique ring carbon atoms fully occupied and the methyl carbon half-occupied. The least-squares refinement included the restraint parameters ISOR 0.01, FLAT 0.005, DFIX 1.40(1) (ring C–C) and 1.48(1) (C–Me) for the toluene solvate in this complex to keep the atoms in this molecule 'nearly isotropic' with expected geometry parameters. The hydrogen atoms of the toluene solvate were ignored; others were included in calculated positions (riding model) with $U_{iso}$ tied to the $U_{eq}$ of the parent atoms. Final *R* [on $F_o > 4\sigma(F_o)$] and *wR* (on all $F^2$) values, respectively, were 0.0410 and 0.0968 for complex **3**. Compound **9** exhibited extensive disorder particularly in the tetraglyme molecule, for which only fourteen of the fifteen non-hydrogen atoms were located from the difference map; these atoms were refined isotropically with C–O and C–C distances constrained at 1.45 and 1.50 Å respectively. The phenyl rings were all treated as idealised hexagons [C–C 1.309 Å, C–C–C (internal) 120.0°]. One of the phenyl rings on a silicon atom was disordered between two distinct orientations (occupancies 0.60 and 0.40). This complex was also associated with half a molecule of toluene per molecule which was refined anisotropically, but with the constraint C–C 1.390 Å. The hydrogen atoms of the tetraglyme moiety and of the toluene hemisolvate were ignored, but those of the phenyls rings on the silicon atoms were included in calculated positions (riding model) with $U_{iso}$ tied to the $U_{eq}$ of the parent atoms. Final *R* [on $F_o > 4\sigma(F_o)$] and *wR* (on all $F^2$) values, respectively, were 0.0642 and 0.1760 for this complex. In the refinement of **9** the Flack parameter[36] had a final value of −0.009(13), which indicated that the absolute crystal structure had been determined correctly. Sources of scattering factors as in ref. 35. The diagrams were drawn with SNOOPI.[37] The calculations were done on a P5-90 pentium personal computer. Crystal data and details of data collection and structure refinements are given in Table 7.

CCDC reference number 186/592.

## Acknowledgements

The authors would like to thank the EPSRC (M. B. H., K. M. A. M., J. A. D. and S. R. D.) for support and BP for endowing D. M. P. M.'s chair, John Barton (mass spectra), Patrick Barrie (solid-state NMR spectra) and Hilary O'Callaghan (microanalysis). Many thanks are also due to Dr. Tim Leedham (Inorgtech) for the gift of Htmhd, and the late Professor Sir Geoffrey Wilkinson and Dr. Paul Lickiss for advice.

## References

1 M. G. Voronkov, E. A. Maletina and V. K. Roman, in *Heterosiloxanes Volume 1: Derivatives of Non-Biogenic Elements*, Harwood Academic, London, 1988.

2 F. T. Edelmann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 586.

3 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.

4 K. G. Caulton, M. H. Chisholm, S. R. Drake and W. E. Strieb, *Inorg. Chem.*, 1990, **29**, 2707.

5 K. G. Caulton, M. H. Chisholm, S. R. Drake and W. E. Strieb, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1483,

6 J. A. Darr, Ph.D. Thesis, University of London, 1995.

7 B. G. Govenlock, W. E. Lindsell and B. Singh, *J. Chem. Soc., Dalton Trans.*, 1978, 657.

8 F. G. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. C. Royo, *J. Chem. Soc., Chem. Commun.*, 1991, 724 and refs. therein.

9 D. Mootz, A. Zinnius and B. Böttcher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 379.

10 M. Krumpolc and V. Chalovsky, *Collect. Czech. Chem. Commun.*, 1972, **32**, 1392.

11 R. Han and G. Parkin, *Polyhedron*, 1990, **9**, 2655; R. Han and G. Parkin, *J. Am. Chem. Soc.*, 1992, **114**, 748.

12 S. R. Drake and D. J. Otway, *Main Group Metal Chem.*, 1991, **14**, 243.

13 K. G. Caulton, M. C. Chisholm, S. R. Drake, K. Folting and W. E. Strieb, *Inorg. Chem.*, 1992, **31**, 3205.

14 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

15 I. Baxter, J. A. Darr, S. R. Drake, M. B. Hursthouse, D. M. P. Mingos and K. M. A. Malik, unpublished work.

16 J. D. Foulon, P. Miele and N. Hovnanian, *Z. Kristallogr.*, 1994, **209**, 282.

17 M. Motevalli, D. Shah, S. A. A. Shah and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1994, 2427.

18 J. A. Darr, S. R. Drake, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 866.

19 V. C. Arunasalam, Ph.D. Thesis, University of London, 1995; D. J. Otway, Ph.D. Thesis, University of London, 1995.

20 Md. A. Hussain, M. B. Hursthouse, Md. A. Mazid and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1988, 1305.

21 Md. A. Hussain, M. B. Hursthouse, Md. A. Mazid, A. Ibrahim and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1989, 2347.

22 C. G. Barraclough, D. C. Bradley, J. Lewis and I. M. Thomas, *J. Chem. Soc.*, 1961, 2601.

23 K. G. Caulton, P. S. Coan, K. Folting, M. J. McGeary and R. C. Wedlich, *Polyhedron*, 1992, **11**, 2459.

24 S. R. Drake, M. B. Hursthouse, K. M. A. Malik and D. J. Otway, *J. Chem. Soc., Dalton Trans.*, 1993, 2883.

25 T. P. Hanusa, *Chem. Rev.*, 1993, **93**, 1023.

26 J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, S. A. S. Miller and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1997, 945.

27 S. R. Drake, M. B. Hursthouse, K. M. A. Malik, and S. A. Miller, *Polyhedron*, 1993, **13**, 1621.

28 J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper and Row, New York, 3rd edn., 1983.

29 See, for example, P. D. Lickiss, S. A. Litster, A. D. Redhouse and C. J. Wisener, *J. Chem. Soc., Chem. Commun.*, 1991, 173; P. D. Lickiss, A. D. Redhouse, K. Rózga, W. A. Stañczyk and R. J. Thompson, *J. Organomet. Chem.*, 1993, **453**, 13.

30 M. A. Hossain, M. B. Hursthouse and K. M. A. Malik, *Acta Crystallogr., Sect. B*, 1978, **35**, 2039.

31 P. S. Coan, L. G. Hubert-Pfalzgraf and K. G. Caulton, *Inorg. Chem.*, 1992, **31**, 1262.

32 P. D. Lickiss and K. M. Stubbs, *J. Organomet. Chem.*, 1991, **421**, 171.

33 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158; adapted for FAST geometry by A. I. Karaulov, University of Wales, Cardiff, 1991.

34 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

35 G. M. Sheldrick, SHELXL 93, program for crystal structure refinement, University of Göttingen, 1993.

36 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

37 K. Davies, SNOOPI, program for crystal structure drawing, University of Oxford, 1983.

*Received* 30*th April* 1997; *Paper* 7/02960H