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A Dimeric Calcium Siloxide Lightly Stabilized by Ammonia Ligands

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The reaction of calcium granules with Ph$_3$SiOH in an ammoniacal–toluene solution at −40 °C produces the complex [Ca$_2$(OSiPh$_3$)$_4$(NH$_3$)$_4$]·0.5C$_7$H$_8$ (**1**), and reaction of compound **1** with thf at room temperature yields [Ca(OSiPh$_3$)$_2$(thf)]$_n$ (**2**). These two compounds were characterized by IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, DSC, and TGA, and the structure of complex **1** was determined by single-crystal X-ray crystallography. The molecule consists of a dimeric calcium motif with one terminal and three μ_2-bridging triphenylsiloxide ligands. The ammonia groups all occupy terminal coordination sites, resulting in asymmetric five- and six-coordinate calcium centers. Crystallographic data for **1** at 150 K: monoclinic space group $P2_1/c$, a = 15.483(7) Å, b = 22.407(5) Å, c = 20.231(7) Å, β = 98.18(2)°, V = 6947.28 Å^3, Z = 4.

Introduction

The first preparations of metal siloxides were reported in the 1870s by Ladenburg for the alkali metals,[2] from the reaction of the metal and respective silanol. Early interest in these materials was restricted to their synthetic utility in silicone polymerization methods.[3] More recently, low-temperature processes have found extensive application to speciality electroceramic materials using molecular precursor strategies. Traditional ceramic preparations require high temperatures in excess of 1000 °C to achieve intimate mixing of the different metal oxide precursor sources. This is normally achieved via the use of either ball milling, hot isostatic pressing, or sol–gel processes. The last process has attracted considerable attention as low-temperature route to ceramics by controlled hydrolysis of well-characterized molecular precursors such as metal alkoxides or siloxides. The advantages of using such materials is that they may be obtained in very high purity (>99.99%), they will generally react at, or just slightly above, room temperature with another molecular precursor, ensuring intimate mixing at the molecular level to yield homogeneous phases.

Metal-containing silicates are finding extensive applications as fibers, powders, or thin films due to their excellent optical, toughness, and insulating properties. We are currently studying the possible application of either alkali or alkaline earth metal siloxides as potential precursors to a wide range of metal oxides and silicates.

Until recently there had been few reports of any alkaline earth metal siloxides. Previous researchers in group IIA metal alkoxide and aryloxide chemistry have noted the propensity and high frequency for metal oxo-based complexes to be obtained, e.g. [HBa$_5$(O)(OPh)$_9$(thf)$_8$],[4] [H$_3$Ba$_6$(O)(OBu^t)$_{11}$(OCEt$_2$CH$_2$O)(thf)$_3$],[4] and [H$_4$Ba$_6$(O)(OCH$_2$CH$_2$OMe)$_{14}$].[5] Given these intrinsic difficulties, Chisholm et al. suggested that the use of siloxides containing the Si–O bond would reduce the possibility of oxo formation (since Si–O cleavage by either a cationic or a radical mechanism is less likely) and may lead to different structural motifs.[7] This was indeed shown to be the case for the complex [Ba$_3$(OSiPh$_3$)$_6$(thf)][7] and also the dimeric compound [Ba$_2$(OSiBut$_3$)$_4$(thf)].[8]

The preparation of group IIA metal siloxides initially posed considerable experimental difficulties since the pK_a of R$_3$SiOH is considerably less than that for the corresponding alcohol. These difficulties were overcome by the use of ammonia-gas-saturated solvents (in this case tetrahydrofuran).[7] This approach leads to barium complexes with metal centers in unusually low coordination environments (e.g. 4 or 5), evidently stabilized by the sterically incumbering ions (i.e. Ph$_3$SiO$^-$ and Bu$^t{}_3$SiO$^-$).

In contrast to the above, the coordination chemistry of either calcium or strontium as their alkoxides or aryloxides is even more underexplored.[6,9–11] Thus we have sought to develop a suitable approach for calcium siloxides, and the initial results are reported herein. Our strategy has yielded a Ca$_2{}^{4+}$ species with differing coordination numbers and an interesting example of siloxide bonding to the two metal centers. We also report preliminary thermal gravimetric analysis and differential scanning calorimetry studies.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen with exclusion of air and moisture. All hydrocarbon and ethereal solvents were dried over 4A molecular sieves, distilled over sodium benzophenone ketyl, and then stored under 4A molecular sieves in an inert atmosphere. NMR solvents were dried over 4A molecular sieves and stored under argon, in glass containers fitted with greaseless J. Youngs valves. Calcium shot and triphenylsilanol were purchased from Alfa Chemicals and Aldrich, respectively, and stored in a inert-atmosphere drybox (Miller Howe 160 FF) under an argon atmosphere. Elemental analyses were performed by Butterworth Laboratories, London. NMR data were recorded on a JEOL GS 270-MHz NMR spectrometer, using the protio impurities of the deuterated solvents as reference for ^{1}H and ^{13}C chemical

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(1) (a) Imperial College of Science, Technology of Medicine. (b) University of Wales College of Cardiff.

(2) Ladenburg, A. *Ber. Dtsch. Chem. Ges.* **1871**, *4*, 901.

(3) Tatlock, W. S.; Rochow, E. G. *J. Am. Chem. Soc.* **1952**, 1555. Hyde, J. F.; Johannson, O. K.; Daudt, W. H.; Fleming, R. F.; Laudenslager, H. B.; Roche, M. P. *J. Am. Chem. Soc.* **1953**, *75*, 5615.

(4) Caulton, K. J.; Chisholm, M. H.; Drake, S. R.; Folting, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1349.

(5) Caulton, K. J.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1498.

(6) Drake, S. R.; Otway, D. J.; Hursthouse, M. B.; Malik, K. M. A. *Polyhedron* **1992**, *11*, 1995.

(7) Caulton, K. J.; Chisholm, M. H.; Drake, S. R.; Streib, W. E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1483.

(8) Drake, S. R.; Streib, W. E.; Folting, K.; Coulton, K. J.; Chisholm, M. H. *Inorg. Chem.* **1992**, *31*, 3205.

(9) Drake, S. R.; Streib, W. E.; Caulton, K. J.; Chisholm, M. H. *Inorg. Chem.* **1990**, *29*, 2707.

(10) Cloke, F. G. N.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1991**, 724. Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1141.

(11) Goel, S. C.; Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. *J. Am. Chem. Soc.* **1991**, *113*, 1844.

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Table I. Crystallographic Data for $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot 0.5C_7H_8$

chem formula	$C_{75.5}H_{76}O_4Si_4Ca_2N_4$ (**1**)	space group	$P2_1/c$
a, Å	15.483(7)	T	150 K
b, Å	22.407(5)	λ(Mo Kα), Å	0.71069
c, Å	20.231(2)	β, deg	98.12(2)
D_c, g cm^{-3}	1.239	V, Å^3	6947.28
μ(Mo Kα), cm^{-1}	2.76	Z	4
R^a	0.0452	fw	1295.96
$R_w{}^b$	0.0518		

^{a} $R = \Sigma(\Delta F)/\Sigma(F_o)$. ^{b} $R_w = \{\Sigma[w(\Delta F)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

shifts. Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer as Nujol mulls between KBr plates, using an O-ring sealed presslock holder (available from Aldrich).

Controlled thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the complexes were done using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a Omni Pro 486DX-33 PC connected to a Rioch 1200 laser printer. The weight of the samples investigated was between 14 and 27 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 mL/min) nitrogen gas, using heating rates of 5 °C/min.

Caution! Liquid ammonia can be extremely dangerous, and hence adequate preparations must be taken. All experiments should be performed in an adequately ventilated fume cupboard, with thick-walled glass Schlenk tubes suitable gas release facilities, and a heavy glass shield.

Synthesis of $[Ca_2(OSiPH_3)_4(NH_3)_4]\cdot 0.5C_7H_8$ (1). Ph_3SiOH (5.52 g, 20 mmol) and toluene (40 mL) were added to calcium granules (0.4 g, 10 mmol) in a Schlenk tube. The reaction mixture was cooled to −40 °C and gaseous ammonia slowly bubbled in for ca. 30 min. The mixture was then left to slowly warm over the next hour with evolution of a large amount of ammonia. The resulting gray suspension was filtered via a 20-mL syringe containing Celite and a glass wool plug as a filtration aid to yield a colorless solution. The solvent was removed under vacuum to yield a waxy solid, which was redissolved in hot toluene (10 mL), the resulting solution was layered with *n*-hexane (15 mL). After 24 h, a small amount of crystals was obtained. Yield: 1.5 g (first crop, 12%). Mp: 110–115 °C, decomposes >165 °C. IR (Nujol; ν cm^{-1}): 3373 (w), 3062 (m), 2923 (vs), 1587 (vw), 1427 (s), 1261 (m), 1109 (vs), 1022 (m), 801 (m), 741 (m), 704 (vs), 519 (s), 456 (w). ^{1}H NMR (270 MHz, 24 °C, C_6D_6): δ −0.64 (s, NH_3), 2.20 (s, Me of toluene), 7.20 (m, Ph para and meta) 7.64 (m, Ph ortho). ^{13}C NMR (67.94 MHz, 24 °C, C_6D_6): δ 128.0 (s, Ph para), 128.7 (s, Ph meta), 135.6 (s, Ph ortho), 142.6 (s, Ph ipso), ^{29}Si NMR (53.57 MHz, C_6D_6, 24 °C): δ −29.3. Anal. Calcd for $Ca_2O_4C_{75.5}H_{76}N_4Si_4$: C, 69.9; H, 5.8; N. 4.3. Found: C, 71.3; H, 6.2; N, 4.7.

Crystal Structure Determination of $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot 0.5C_7H_8$. A summary of crystallographic data for complex **1** is given in Table I. The X-ray measurements were made on a crystal of approximate dimensions 0.40 × 0.35 × 0.20 mm, mounted using silicone oil and transferred to the goiniostat. The data were collected at 150 K on a Delft Instruments FAST TV area detector diffractometer equipped with a rotating anode FR591 generator (50 kV, 50 mA), a bufferboard, a DEP image intensifier with Mo Kα radiation (λ = 0.170 69 Å, graphite monochromator), and an Oxford Cryostream low-temperature cooling system, controlled by a microVAX 3200 and driven by MADNES[12] software. The orientation matrix and unit-cell parameters were determined *via* the ENDEX and REFINE routines of the MADONL software (the small-molecule version of MADNES) using 50 reflections from two 5° FIND rotation ranges separated by 90° around an arbitary axis and subsequently refined during data processing using 250 reflections from each processed batch of data. Data evaluation was performed off-line on a VAX station 4000/60 clustered with the diffractometer driving computer, with frame transfer and processing taking place simultaneously with data collection. Slightly more than one hemisphere of data were collected (an ω rotation of 195° around an arbitary axis at $\chi = 0°$ plus two complementary "cusps" of 70°, each differing by 90° in φ at $\chi = 90°$ with crystal to detector distances = 39.96 mm, detector swing angle = 24.97°, between frames increment = 0.20°, and exposure time = 10 s).

Table II. Selected Bond Distances (Å) and Angles (deg) for $[Ca_2(OSiPh_3)_4(NH_3)_4]$

Ca(2)···Ca(1)	3.129(4)	O(1)–Ca(1)	2.334(5)
O(2)–Ca(1)	2.462(5)	O(3)–Ca(1)	2.325(5)
O(4)–Ca(1)	2.179(5)	N(1)–Ca(1)	2.598(9)
N(2)–Ca(1)	2.568(8)	O(1)–Ca(2)	2.269(5)
O(2)–Ca(2)	2.251(5)	O(3)–Ca(2)	2.275(5)
N(3)–Ca(2)	2.537(7)	N(4)–Ca(2)	2.543(8)
O(1)–Si(1)	1.590(5)	C(1)–Si(1)	1.877(6)
C(7)–Si(1)	1.891(7)	C(13)–Si(1)	1.881(6)
O(2)–Si(2)	1.590(5)	C(19)–Si(2)	1.889(7)
C(25)–Si(2)	1.890(6)	C(31)–Si(2)	1.878(7)
O(3)–Si(3)	1.596(6)	C(37)–Si(3)	1.885(8)
C(43)–Si(3)	1.872(7)	C(49)–Si(3)	1.861(8)
O(4)–Si(4)	1.578(5)	C(55)–Si(4)	1.897(7)
C(61)–Si(4)	1.865(8)	C(67)–Si(4)	1.880(7)
O(2)–Ca(1)–O(1)	75.1(2)	O(3)–Ca(1)–O(1)	80.0(2)
O(3)–Ca(1)–O(2)	76.5(2)	O(4)–Ca(1)–O(1)	99.3(2)
O(4)–Ca(1)–O(2)	170.5(1)	O(4)–Ca(1)–O(3)	110.4(2)
N(1)–Ca(1)–O(1)	164.5(2)	N(1)–Ca(1)–O(2)	104.2(3)
N(1)–Ca(1)–O(3)	84.8(3)	N(1)–Ca(1)–O(4)	83.2(3)
N(2)–Ca(1)–O(1)	117.1(3)	N(2)–Ca(1)–O(2)	91.0(2)
N(2)–Ca(1)–O(3)	155.8(2)	N(2)–Ca(1)–O(4)	84.8(2)
N(2)–Ca(1)–N(1)	78.3(3)	O(2)–Ca(2)–O(1)	80.7(2)
O(3)–Ca(2)–O(1)	82.5(2)	O(3)–Ca(2)–O(2)	81.8(2)
N(3)–Ca(2)–O(1)	91.9(2)	N(3)–Ca(2)–O(2)	164.8(2)
N(3)–Ca(2)–O(3)	110.4(2)	N(4)–Ca(2)–O(1)	137.9(2)
N(4)–Ca(2)–O(2)	96.6(2)	N(4)–Ca(2)–O(3)	139.1(2)
N(4)–Ca(2)–N(3)	80.0(3)		
C(1)–Si(1)–O(1)	108.9(3)	C(7)–Si(1)–O(1)	112.3(3)
C(7)–Si(1)–C(1)	106.6(3)	C(13)–Si(1)–O(1)	112.1(3)
C(13)–Si(1)–C(1)	107.2(3)	C(13)–Si(1)–C(7)	109.5(3)
C(19)–Si(2)–O(2)	110.7(3)	C(25)–Si(2)–O(2)	112.4(3)
C(25)–Si(2)–C(19)	104.9(3)	C(31)–Si(2)–O(2)	111.4(3)
C(31)–Si(2)–C(19)	110.5(3)	C(31)–Si(2)–C(25)	106.8(3)
C(37)–Si(3)–O(3)	106.4(3)	C(43)–Si(3)–O(3)	111.3(3)
C(43)–Si(3)–C(37)	110.1(3)	C(49)–Si(3)–O(3)	114.3(4)
C(49)–Si(3)–C(37)	107.3(4)	C(49)–Si(3)–C(43)	107.3(4)
C(55)–Si(4)–O(4)	112.0(3)	C(61)–Si(4)–O(4)	112.8(3)
C(61)–Si(4)–C(55)	107.3(3)	C(67)–Si(4)–O(4)	112.8(3)
C(67)–Si(4)–C(55)	106.1(3)	C(67)–Si(4)–C(61)	105.4(3)
Ca(2)–O(1)–Ca(1)	85.6(2)	Si(1)–O(1)–Ca(1)	139.2(2)
Si(1)–O(1)–Ca(2)	132.3(2)	Ca(2)–O(2)–Ca(1)	83.1(2)
Si(2)–O(2)–Ca(1)	134.0(2)	Si(2)–O(2)–Ca(2)	142.5(2)
Ca(2)–O(3)–Ca(1)	85.7(2)	Si(3)–O(3)–Ca(1)	151.4(2)
Si(3)–O(3)–Ca(2)	122.6(3)	Si(4)–O(4)–Ca(1)	162.9(2)

The total of 35 393 intensities measured within the θ range 2.2–29.9° yielded 15 949 unique and 5778 observed [$F_o > 4\sigma(F_o)$] reflections (merging R = 0.074). The data were corrected for Lorentz and polarization effects and also for absorption using the program DIFABS.[13] The structure was solved by direct methods (MULTAN)[14] and refined (all nonhydrogen atoms anisotropic) by full-matrix least-squares routines (SHELX-80)[15] to give a final R value of 0.0452 for 5778 observed data and 830 parameters. A disordered toluene molecule (solvent of crystallization) was present in the void around a center of symmetry; for this toluene, six independent carbon positions with fixed partial occupancies were refined anisotropically. The hydrogen atoms belonging to the phenyl rings of the $OSiPh_3$ groups were allowed to ride on their parents in calculated positions (C–H = 0.96 Å), and a common U_{iso} was refined for all. The hydrogen atoms in the ammonia and disordered toluene molecules were ignored. The refinement was based on F_o, and each reflection was assigned unit weight since this gave flat analyses of variance with (F_o/F_{max}). The minimum and maximum residual electron densities in the final difference map were 0.31 and 0.34 e Å^{-3}.

All calculations were performed on a T800 transputer hosted by an IBM/AT personal computer. Final atomic parameters are given in Table II; selected bond lengths and angles, in Table III. The structure of a single molecule of complex **1** is shown in Figure 2, and the $Ca_2O_4N_4$ core, in Figure 3.

Synthesis of $[Ca(OSiPh_3)_2(thf)]_n$ (2). Ph_3SiOH (5.52 g, 20 mmol) and thf (40 mL) were added to Ca (0.4 g, 10 mmol) in a Schlenk tube.

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(12) Pflugrath, J. W.; Messerschmidt, A. MADNES, version Jan 1990, distributed by Delft Instruments, Delft, The Netherlands.

(13) Walker, N. P. C.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 1980 (adapted for FAST geometry by A. Karaulov, University of Wales College of Cardiff, 1991).

(14) Debaerdemaeker, T.; Germain, G.; Main, P.; Tate, C.; Woolfson, M. M. MULTAN-87, Program for Crystal Structure Determination. University of York, U.K., 1987.

(15) G. M. Sheldrick, University of Gottingen, 1980 (scattering factor data as included in the SHELX-S program (G. M. Sheldrick, University of Gottingen, Germany, 1986).

Table III. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot0.5C_7H_8$

	x	y	z	U_{eq}		x	y	z	U_{eq}
Ca(1)	2550.1(6)	26.4(4)	7736.8(4)	29.1(3)	C(33)	5032(4)	−2365(3)	8579(3)	74(2)
Ca(2)	1964.9(7)	−728.1(4)	6449.6(5)	31.9(3)	C(34)	5595(4)	−1958(3)	8349(4)	80(2)
Si(1)	244.5(8)	107.9(5)	6973.3(6)	25.4(4)	C(35)	5241(5)	−1473(3)	7986(4)	84(2)
Si(2)	2567.4(9)	−1636.0(6)	7937.8(6)	29.7(4)	C(36)	4339(4)	−1380(3)	7884(3)	53(2)
Si(3)	3778.2(9)	73.5(7)	6237.8(7)	39.9(5)	C(37)	3644(4)	−508(2)	5557(3)	53(1)
Si(4)	2667.5(9)	1589.6(6)	8358.1(7)	34.4(4)	C(38)	3702(6)	−1103(3)	5729(4)	108(2)
O(1)	1252(2)	−43(1)	6997(1)	29(1)	C(39)	3572(8)	−1555(4)	5252(6)	147(2)
O(2)	2360(2)	−1048(1)	7504(2)	33(1)	C(40)	3386(7)	−1415(4)	4614(6)	128(2)
O(3)	3108(2)	−98(2)	6738(2)	38(1)	C(41)	3286(5)	−842(4)	4405(4)	94(2)
O(4)	2504(2)	970(1)	7991(2)	40(1)	C(42)	3425(4)	−391(3)	4882(3)	63(1)
N(1)	4175(4)	126(3)	8263(3)	107(2)	C(43)	3544(3)	833(2)	5871(2)	35(1)
N(2)	2459(4)	−148(2)	8980(2)	77(2)	C(44)	3973(4)	1060(2)	5358(3)	45(1)
N(3)	1120(4)	−430(2)	5331(2)	61(1)	C(45)	3768(4)	1619(3)	5092(3)	52(2)
N(4)	1666(4)	−1753(2)	5927(2)	72(1)	C(46)	3152(4)	1971(3)	5339(3)	52(1)
C(1)	−418(3)	−515(2)	6537(2)	29(1)	C(47)	2743(4)	1764(2)	5855(3)	49(2)
C(2)	−118(3)	−1100(2)	6621(2)	38(1)	C(48)	2936(3)	1201(2)	6116(3)	44(1)
C(3)	−551(4)	−1577(2)	6293(3)	51(1)	C(49)	4944(4)	65(4)	6623(3)	75(2)
C(4)	−1308(4)	−1483(2)	5863(3)	48(1)	C(50)	5273(6)	517(6)	6990(5)	165(2)
C(5)	−1639(3)	−914(2)	5763(2)	41(1)	C(51)	6163(9)	542(8)	7303(6)	221(2)
C(6)	−1200(3)	−440(2)	6100(2)	35(1)	C(52)	6614(7)	38(7)	7223(7)	175(2)
C(7)	−85(3)	167(2)	7836(2)	27(1)	C(53)	6384(7)	−384(6)	6798(6)	161(2)
C(8)	432(3)	477(2)	8342(2)	33(1)	C(54)	5532(5)	−366(5)	6507(5)	119(2)
C(9)	215(4)	501(2)	8986(2)	39(1)	C(55)	2176(3)	1615(2)	9165(2)	34(1)
C(10)	−518(4)	214(2)	9132(2)	40(1)	C(56)	2544(4)	1312(3)	9735(3)	52(1)
C(11)	−1048(3)	−93(2)	8638(2)	40(1)	C(57)	2173(5)	1347(3)	10327(3)	78(2)
C(12)	−825(3)	−116(2)	8001(2)	36(1)	C(58)	1424(6)	1676(3)	10342(4)	86(2)
C(13)	−73(3)	812(2)	6493(2)	29(1)	C(59)	1049(5)	1962(3)	9784(4)	69(2)
C(14)	472(4)	1044(2)	6060(2)	38(1)	C(60)	1423(4)	1938(2)	9206(3)	44(1)
C(15)	250(4)	1560(2)	5691(3)	55(1)	C(61)	3850(4)	1773(2)	8568(3)	49(1)
C(16)	−522(5)	1845(2)	5742(3)	61(1)	C(62)	4284(4)	1938(3)	9192(4)	70(2)
C(17)	−1070(4)	1630(2)	6164(3)	57(2)	C(63)	5154(5)	2073(4)	9299(4)	105(2)
C(18)	−849(4)	1112(2)	6535(3)	42(1)	C(64)	5628(5)	2055(5)	8785(5)	141(2)
C(19)	2063(3)	−1594(2)	8734(2)	32(1)	C(65)	5235(6)	1885(5)	8166(5)	152(2)
C(20)	1237(4)	−1338(2)	8717(3)	46(1)	C(66)	4368(5)	1743(4)	8059(4)	109(2)
C(21)	829(4)	−1293(3)	9277(3)	54(1)	C(67)	2175(4)	2233(2)	7840(2)	38(1)
C(22)	1235(4)	−1509(3)	9881(3)	56(2)	C(68)	2489(5)	2811(2)	7921(3)	63(2)
C(23)	2035(4)	−1761(2)	9918(3)	51(1)	C(69)	2082(5)	3289(3)	7559(3)	79(2)
C(24)	2448(4)	−1801(2)	9351(3)	42(1)	C(70)	1334(5)	3199(3)	7121(3)	64(2)
C(25)	2078(3)	−2326(2)	7497(2)	30(1)	C(71)	1026(4)	2637(3)	7014(3)	56(1)
C(26)	1184(3)	−2447(2)	7430(3)	38(1)	C(72)	1442(4)	2157(2)	7372(3)	45(1)
C(27)	819(4)	−2945(2)	7091(3)	48(2)	C(73)[a]	3488(15)	−102(13)	837(12)	182(2)
C(28)	1327(4)	−3337(2)	6809(3)	48(1)	C(74)[a]	4211(11)	−30(10)	395(8)	125(2)
C(29)	2204(4)	−3233(2)	6856(3)	55(2)	C(75)[a]	4434(13)	−656(9)	121(10)	154(2)
C(30)	2577(4)	−2733(2)	7198(3)	48(1)	C(76)[a]	4599(13)	352(9)	374(11)	143(2)
C(31)	3774(3)	−1770(2)	8132(2)	37(1)	C(77)[a]	5090(14)	−672(9)	−278(9)	134(2)
C(32)	4146(4)	−2271(3)	8473(3)	53(1)	C(78)[a]	4640(15)	−304(10)	203(12)	160(2)

[a] Atoms in disordered toluene molecule, refined with fixed partial occupancies: C(73), 0.5; C(74), 0.6; C(75), 0.6; C(76), 0.6; C(77), 0.6; C(78), 0.6.

The reaction mixture was cooled to −40 °C and gaseous ammonia slowly bubbled in for ca. 30 min. The mixture was then left to slowly warm over the next hour with evolution of a large amount of ammonia. The resulting gray suspension was filtered via a 20-mL syringe containing Celite and glass wool as a filtration aid to yield a colorless solution. The solvent was removed under vacuum to yield a waxy solid, which was redissolved in hot toluene (10 mL), and the resulting solution was layered with *n*-hexane (15 mL). After 24 h, a large amount of crystals was obtained. Yield: 4.8 g (first crop, 72.1%). Mp: desolvates 120–125 °C. IR (Nujol; ν, cm^{-1}): 3373 (w), 3132 (m), 2922 (vs), 1587 (m), 1428 (s), 1261 (m), 1184 (m), 1105 (s), 1068 (m), 1020 (s), 991 (m), 856 (m), 739 (m), 699 (s), 563 (s), 422 (w). ^1H NMR (270 MHz, 24 °C, C_6D_6): δ 1.58 (m, thf), 2.20 (s Me), 3.6 (m, thf), 7.29 (m, Ph para and meta), 7.96 (d, Ph ortho). ^{13}C NMR (67.94 MHz, 24 °C, pyridine-d_5): δ 127.6 (s, Ph para), 128.2 (s, Ph meta), 136.1 (s, Ph ortho), 145.2 (s, Ph ipso). ^{29}Si NMR (53.57 (MHz, pyridine-d_5, 24 °C): δ −32.6. Anal. Calcd. for $Ca_2O_4C_{75.5}H_{76}N_4Si_4$: C, 69.4; H, 5.8; N, 4.3. Found: C, 69.8; H, 6.2; N, 4.5.

Results and Discussion

Synthesis and Characterization. The extent of dissolution of the heavier alkaline earth metals in alcohols has been shown to be dramatically increased by the addition of ammonia gas either at room temperature[7,8] or at −40 °C to yield a mixed organic–ammoniacal solution.[6,9,16] We have sought to prepare a homoleptic calcium siloxide complex by the reaction of calcium metal shot and Ph_3SiOH and a mixed ammoniacal–toluene solution at −40 °C.

We have found that there is no reaction between the metal shot and silanol even after several days' reflux. Thus the ammonia in this case not only acts as a solubilizing reagent for the calcium in tandem with the toluene but, most importantly, acts as an effective Lewis base to yield a toluene-soluble colorless crystalline solid, $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot0.5C_7H_9$ (**1**). If the same reaction was performed in the polar solvent tetrahydrofuran, a facile high-yield reaction occurred to give the thf adduct $[Ca(OSiPh_3)_2(thf)]_n$ (**2**). The higher yield and greater solubility of complex **2** may possibly be attributed to several of the following factors. We have previously noted[16] that the mixed ammoniacal–ethereal solvents have a far greater solubilizing effect on the heavier alkaline earth metals, than have the corresponding ammoniacal–hydrocarbon solvents. This is probably due to the improved dielectric constant and solvating ability of the ethereal solvent versus that of the toluene; similar solvent effects have also been observed for the heavier alkali metals. The group IIA metals also appear to prefer an "O–O" rather than a mixed "O–N" coordination

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[16] Drake, S. R.; Otway, D. J. *Polyhedron* **1992**, *11*, 745; *J. Chem. Soc., Chem. Commun.* **1991**, 517.

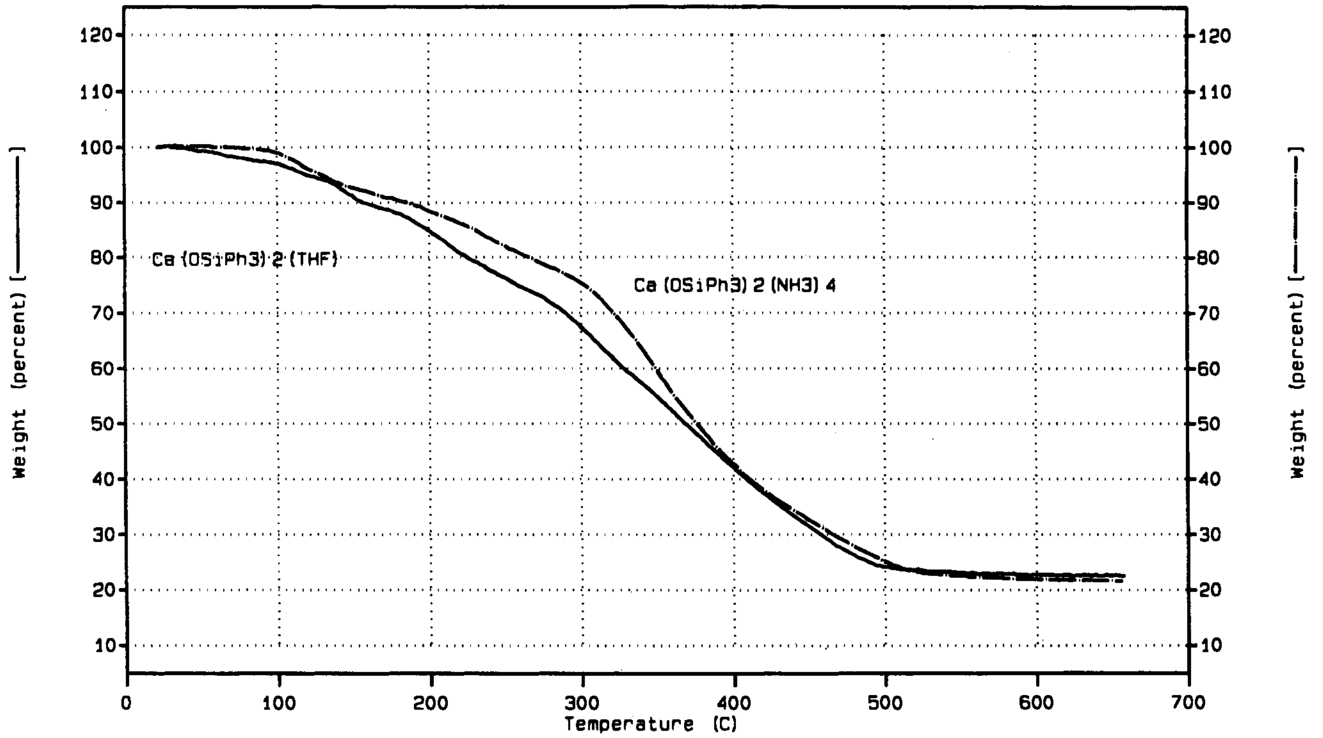

Figure 1. Thermogravimetric analysis plots for complexes **1** and **2**.

environment. This effect has been studied by us and other researchers and shown to result in greater solubility and higher stability for the complexes.[17]

Spectroscopic Studies. The infrared spectrum of complex **1** reveals a sharp peak at 3373 cm^{-1}, which is attributed to an N–H stretching vibration in the coordinated ammonia. Likewise, compound **2** has a peak at 1068 cm^{-1} due to a C–O–C vibration of the coordinated thf Lewis base ligand.

The ^{1}H NMR spectra of the two compounds in noncoordinating solvents clearly show the presence of NH_3 ligands in **1** and thf in **2**. The corresponding ^{13}C NMR spectra show peaks which may be attributed to only one single type of phenyl environment. Previous researchers have shown that ^{29}Si NMR may be used as a very powerful and discriminating tool for probing ^{29}Si environments, e.g. in $Ba_3(OSiPh_3)_6(thf)$[7] and $KBa_2(OSiPh_3)_5(dme)$.[17] The resolution was such that differentiation among terminal, bridging, and μ_3 capping siloxide ligands was achieved. In the present study, this has not proved to be possible with only one broad ^{29}Si signal observed irrespective of the solvent used (e.g. C_6D_6 or C_5D_5N). This indicates a strong possibility of Ph_3SiO^- bridging and terminal ligand site exchange in these molecules.

Thermal Gravimetric Analysis. The thermogravimetric graph (see Figure 1) for complex **1** is more or less continuous within the temperature range 85–520 °C, but the first derivative clearly identifies at least three major overlapping reactions at (i) 85–160 °C, (ii) 160–270 °C, and (iii) 270–520 °C. The presence of three reactions in the thermal decomposition of the complex is also supported by the presence of the corresponding endotherms, which are rather broad, in the DSC curve at (i) 50–180 °C, (ii) 180–250 °C, and (iii) 250–415 °C. The first reaction corresponds to the simultaneous expulsion of the lattice toluene (half a molecule) and the four ammonia molecules, with an observed weight loss of 8% (calculated 7.5%). The loss of the lattice component at fairly low temperature is expected, but the fact that the four ammonia molecules bonded to calcium are also lost at low temperatures clearly indicates that these species are very weakly bonded to the metals. In fact, the weak nature of the Ca–NH_3 bonds has also been confirmed by our X-ray results. The natures of the second and third reactions are less clearly understood although these possibly involve the loss of the phenyl groups.

Complex **2** shows behavior related to that of compound **1** with the first-derivative TGA plot exhibiting strong evidence for three major overlapping reactions at (i) 70–160 °C, (ii) 175–270 °C, and (iii) 270–400 °C. These isotherms are also supported by related peaks in the corresponding DSC spectrum. Similar comments may be made as to the identity of the first-reaction component, which is most likely to be loss of the tetrahydrofuran, with a weight loss of 9.8% (calculated 10.5%). The loss of the Lewis base at relatively low temperature is in accord with our observations for the loss of ammonia from **1** and suggests the weak nature of the M–O bond to this ligand.

These thermogravimetric results suggest a pronounced lability and relatively weak coordination of Lewis base coligands to the calcium siloxide framwork; thus the first product which forms is most likely to be an oligomeric $[Ca(OSiPh_3)_2]_\infty$ material.

The above processes are also in accord with mass spectrometry studies, which clearly show for these complexes evolution of either NH_3 or thf ligands occurs, and this is a facile process at 100 °C as studied by electron impact mass spectrometry.

X-ray Diffraction Study of $[Ca_2(OSiPh_3)_4(NH_3)_4]$. The complex $[Ca_2(OSiPh_3)_4(NH_3)_4]$ (**1**) crystallizes with a half-molecule of toluene per complex molecule in the crystal lattice. The molecular structure (Figure 2) adopted is that containing one terminally bonded and three μ_2-bridging siloxides. The environments of the two calcium metal centers are inequivalent, due to the different ligand dispositions. Thus Ca(1) is bound to the fourth siloxide ligand O(4) and to two terminal ammonia ligands, while Ca(2) binds to only two terminal ammonia ligands. This gives rise to six- and five-coordinate metal centers. Ca···Ca nonbonded distance for the dimer is 3.129(4) Å.

This structural motif involves suitable comparison with the recently reported structures of barium alkoxide, $[Ba_2(OCPh_3)_4(thf)_3]$,[8] and the siloxides $[Ba_3(OSiPh_3)_6(thf)]$[7] and $[Ba_2(OSiBu^t_3)_4(thf)]$.[8] Complex **1** adopts a structure which resembles closely that of an M_2X_9 face-shared bioctahedron, with only one terminal ligand removed. This result in Ca(1) being in a highly distorted octahedral geometry and in Ca(2) having a square-

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(17) Coan, P. S.; Streib, W. E.; Caulton, K. J. *Inorg. Chem.* **1991**, *30*, 5019.

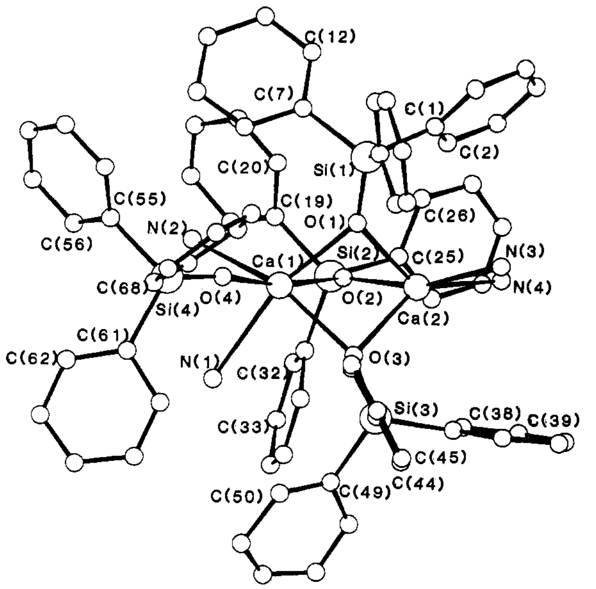

Figure 2. Molecular structure of $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot 0.5C_7H_8$ (**1**) showing the atom-numbering scheme. H atoms have been omitted for clarity.

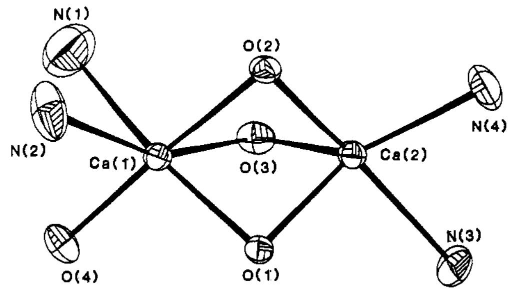

Figure 3. Structure of the $Ca_2O_4N_4$ central core.

pyramidal coordination. These two coordination polyhedra share a triangular face defined by a basal edge O(1) and O(2) and an apex O(3) (see Figure 3). Any possible space "below" calcium 2 is hindered by two phenyl rings from different bridging ligands [on O(1) and O(2)]. There are no contacts from calcium to either C or H that would qualify as even presumably weak bonds; Ca(2)- - -C(2) is 3.396(5) Å and Ca- - -H(2) is 2.89(2) Å, and the shortest observed nonbonded Ca(2)- - -C(38) contact is 3.343(5) Å. Similar observations were also noted for the related barium alkoxide and siloxide complexes.

The Ca-(μ-$OSiPh_3$) distances fall into a relatively small range 2.252(5)–2.334(5) Å, with only the Ca(1)–O(2) bond being slightly longer at 2.462(5) Å; this latter bond is trans to the terminal siloxide ligand, which has the shortest M–O distance [2.179(5) Å] in the entire molecule. A situation comparable to this was also noted in $Ba_2(OCPh_3)_4(thf)_3$.

The Ca–O–Ca angles involving the bridging ligands are similar, 83.1(2), 85.6(2), and 85.7(2)°, but the Ca–O–Si angles show large variations: 132.3(2), 139.2(2)° at O(1); 134.0(2), 142.5(2)° at O(2); and 122.6(2), 151.4(2) at O(3). The Ca–O–Si angle involving the terminal ligand is much larger, 162.9(2)°. These angular variations are probably due to interligand interactions. The three oxygens are all nearly planar, as shown by the sums of their interbond angles, i.e. 357.1(2)° [O(1)], 359.6(2)°, [O(2)], and 359.7(2) [O(3)].

The Ca–N(NH_3) bond distances lie in range 2.537(7)–2.598(9) Å, values much larger than what would be expected from the sum of the covalent radii. It is also significant that the average Ca–N distance, 2.568(2) Å, is about 0.27 Å longer than the average Ca–O distance, 2.299(2) Å, although the covalent radius of nitrogen is only about 0.02 Å larger than that of oxygen. This clearly indicates that the Ca–NH_3 bonds in the present complex are quite weak, which is also consistent with the facile loss of the ammonia molecules along with the lattice toluene at the initial stage of thermal decomposition (vide TGA curve, Figure 1).

Discussion

The structure we report here for $[Ca_2(OSiPh_3)_4(NH_3)_4]\cdot 0.5C_7H_8$ shares similar features with those of $[Ba_2(OCPh_3)_4(thf)_3]$ and $[Ba_2(OSiBu^t_3)_4(thf)]$.[7,8] All of the complexes have the same $XM(\mu\text{-}X)_3M$ structural motif, as found in $XSn^{II}(\mu\text{-}X)_3M'$ complexes.[18] Such structures are still relatively uncommon; indeed, the majority of dimeric complexes are far more likely to adopt the symmetric structure observed in $Co(OCPh_3)_4$.[19] It was previously suggested that the controlling factors for the formation of such a structure are the presence of three bulky bridging alkoxide groups and, further, a large cationic repulsion between the two cations. Calcium has an ionic radius of 1.06 Å; although smaller than that of barium (1.35 Å), it is still noticeably larger than that for cobalt (0.745 Å). Thus three, rather than two, bridging anions are required to shield the repulsion and develop a net attractive force toward the midpoint. It has also been noted that the presence of three bridging ligands effectively increases the coordination number of barium with minimum intramolecular repulsion. We would further suggest that this structural motif appear to be unaffected by the nature or the size of Lewis base used, i.e. NH_3 or thf.

Surprisingly ^{29}Si NMR studies have shown that the siloxide complexes **1** and **2** are not stereochemically rigid, and site exchange of $^-OSiPh_3$ ligands may occur. These data suggest that the double-bridged intermediate $OCa(\mu\text{-}O)_2CaO$ must be at an energy similar to that of the tribridged species crystallographically characterized.

Complex **1** nicely illustrates that the alkaline earth alkoxides and siloxides prefer to form uncharged molecular species, to the nearly complete exclusion of charge-separated salts.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations and figures showing thermogravimetric analysis (first derivative) and DSC curves (11 pages). Ordering information is given on any current masthead page.

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(18) Veith, M.; Rosler, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *21*, 858.

(19) Sigel, G. A.; Bartlett, R. A.; Decker, D. A.; Olstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773.