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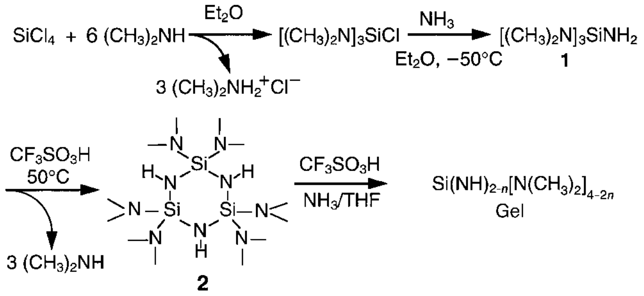
Non-Oxide Sol–Gel Chemistry: Preparation from Tris(dialkylamino)silazanes of a Carbon-Free, Porous, Silicon Diimide Gel

Riccardo Rovai, Christian W. Lehmann, and
John S. Bradley*

Sol–gel chemistry plays an important role in the preparation and processing of oxide materials, including microporous oxides and dense ceramics.[1, 2] There are few examples of non-oxide sol–gel techniques,[3–5] and the only reported sol–gel preparation in silicon–nitrogen chemistry is the synthesis of a Si/C/N solid by the reaction of methyltrichlorosilane with bistrimethylsilylcarbodiimide to form a nonporous gel in which the structural framework contains only SiNCNSi units.[6, 7] We are attempting to apply the chemistry of silicon amide compounds to the development of a "chimie douce" methodology for carbon-free SiM(NH)$_x$ gels (M = Si or metal), to give a sol–gel route to non-oxide ceramics and provide an alternative, mild synthetic route to nitridosilicates.[8–10] Such gels would be the azo analogues of silica-based amorphous oxide gels, and the nitridosilicate analogue to silica gel would be a gel of silicon diimide (Si(NH)$_2$). A putative imide/nitride pathway can be envisioned in which dialkylamido compounds of silicon are subjected to ammonolysis and condensation to an imide.

The reactions of Si(NR$_2$)$_4$ compounds, and of bimetallic analogues, with ammonia have been reported to give amorphous powders[11–16] and, in OMCVD experiments, silicon nitride films.[17] However, silicon diimide gels have not been reported from these or any other starting materials. We report here the preparation of a silicon imide gel by acid-catalyzed ammonolysis of the hitherto unreported tris(dimethylamino)-silylamine [(CH$_3$)$_2$N]$_3$SiNH$_2$, **1**, which we have prepared from silicon tetrachloride in high yield and purity. The probable first step in this process is the acid-catalyzed self-condensation of **1** to the cyclic trimer [{(CH$_3$)$_2$N}$_2$SiNH]$_3$ (**2**), for which we report the X-ray crystal structure. The acid-catalyzed ammonolysis of **2**, or the equivalent sequential self-condensation and ammonolysis of **1**, under mild conditions, yields a semirigid translucent gel. On drying under mild conditions in an ammonia atmosphere this non-oxide gel yields a high surface area silicon diimide xerogel, the first example of a porous non-oxide silicate gel.

Compound **1** was prepared in high yield from silicon tetrachloride (Scheme 1) as a colorless liquid, and characterized by elemental analysis, IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies, and mass spectrometry. It can be distilled under atmospheric pressure without detectable decomposition. Compound **1** is the simplest member of the series (R$_2$N)$_n$Si(NH$_2$)$_{(4-n)}$ (R = Me, n = 3), and is one of very few examples of a tris(amido)silylamine yet reported.[18] We have also prepared tris(morpholino)silylamine as a crystalline solid analogue to **1**. Details of the synthesis and structure of this compound will be published separately.



Scheme 1. Synthesis of **1** and **2** as well as the translucent gel of the composition Si(NH)$_{2-n}$[N(CH$_3$)$_2$]$_n$.

When **1** is heated in the presence of excess ammonia under autogenous pressure (100 bar) at 110 °C, a white powder is obtained, which is shown by IR spectroscopy to be Si(NH)$_2$.[19] The material is of low surface area ($<50\,m^2g^{-1}$), and is presumably identical to the powder prepared by Union Carbide workers by the acid-catalyzed ammonolysis of (Me$_2$N)$_4$Si.[11] However, when **1**, either neat or in THF, is treated at 50 °C with a catalytic amount of trifluoromethanesulfonic acid, self-transamination occurs with loss of dimethylamine to give predominantly the cyclic trimer **2** (80 % according to MS, 61 % after recrystallization; Scheme 1). Compound **2** has been previously described as a product of the reaction of (Cl$_2$SiNH)$_3$ (a by-product (3 % yield) of the

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[*] Prof. Dr. J. S. Bradley
Department of Chemistry
University of Hull
Cottingham Road, Hull, HU6 7RX (UK)
E-mail: J.S.Bradley@chem.hull.ac.uk
Dipl.-Chem. R. Rovai, Dr. C. W. Lehmann
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr (Germany)

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reaction of ammonia with silicon tetrachloride) with dimethylamine, but neither its structure nor reaction chemistry have been reported.[20, 21] The molecular structure of **2** was determined by X-ray diffraction (Figure 1). The compound is made up of a six-membered Si_3N_3 ring in which each of the three Si atoms is bound to two exocyclic nitrogen atoms of dimethylamino groups and two endocyclic NH groups to provide an SiN_4 environment. The mean deviation of Si and N atoms from a plane through the six-membered ring is 0.105 Å. The sums of the interatomic angles at the three endocyclic nitrogen atoms are 360.0° (N7), 360.1° (N8), and 359.9° (N9), which reflect the essential planarity of these nitrogen atoms.

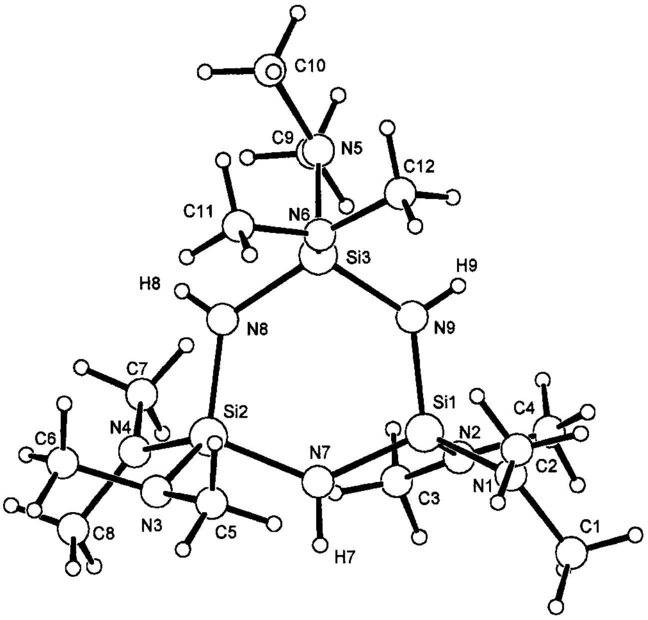

Figure 1. Crystal structure of **2**. Selected bond lengths [nm] and angles [°]: Si1–N1 0.1717(2), Si1–N2 0.1716(2), Si1–N7 0.1722(1), Si1–N9 0.1723(2), Si2–N3 0.1736(2), Si2–N4 0.1718(2), Si2–N7 0.1718(2), Si2–N8 0.1715(2), Si3–N5 0.1730(2), Si3–N6 0.1713(2), Si3–N8 0.1717(2), Si3–N9 0.1710(2), N7–H7 0.091(2), N8–H8 0.073(2), N9–H9 0.081(2); N9-Si1-N7 106.2(1), N8-Si2-N7 105.3(1), N9-Si3-N8 107.1(1), Si2-N7-H7 113.6(13), Si1-N7-H7 113.1(13), Si2-N8-H8 116.3(19), Si3-N8-H8 112.8(19), Si1-N9-H9 116.4(16), Si3-N9-H9 112.8(16).

When the mixture obtained by acid-catalyzed self-condensation of **1** in THF is exposed to ammonia, gelation occurs with further loss of dimethylamine to give a semirigid, dimensionally stable, translucent gel. The intermediacy of **2** in the ammonolysis of **1** is demonstrated by rapid gel formation on exposure to ammonia of a solution of pure **2** in THF containing 1 mol% of trifluoromethanesulfonic acid. It seems that four equivalents of ammonia are needed to cause rapid gelation, instead of the three equivalents which the stoichiometry of the ammonolysis reaction would require. When a gel obtained in this manner in a cylindrical glass mould was dried slowly over a period of several days under an atmosphere of argon that was constantly replaced, it shrunk from the walls of the mould but retained its cylindrical form before cracking after about 50% linear shrinkage. We have as yet made no attempt to optimize the drying procedure to obtain fully dried monoliths, and the effect of changes in gelation conditions, and of variation of the alkyl substituent in the tris(dialkyamido)siliylamine starting material, are under investigation.

The xerogel produced by drying under reduced pressure, which has a Brunauer–Emmett–Teller (BET) surface area of about 1000 $m^2 g^{-1}$, contains residual dimethylamino groups, as shown by the presence of ν(CH) bands in the IR spectrum of the dried material. A low-intensity shoulder (3475 cm^{-1}) on the principal ν(NH) band (3362 cm^{-1}) and a low-intensity band at 1551 cm^{-1} in the IR spectrum of the dried gels are assigned to the $\nu(NH_2)$ and $\delta(NH_2)$ bands of $SiNH_2$ groups. The presence of these bands suggests that the condensation reaction was not yet complete by the time rigid gel formation was observed. Thermogravimetric analysis in combination with mass spectrometry (TGA/MS; argon stream, 5 °C min^{-1}, 25–900 °C) of the gels shows only loss of dimethylamine and ammonia, which are expected to be eliminated as the condensation reaction goes to completion. Treatment of the gel under flowing ammonia at 50 °C for 15 h removes all dimethylamino groups. The IR spectrum of the resulting solid shows only ν(NH), $\nu(NH_2)$, $\delta(NH_2)$, and Si–N absorbances, and thus identifies the resulting white amorphous solid (surface area 500 $m^2 g^{-1}$) as a porous, carbon-free silicon diimide gel containing terminal NH_2 groups.

The imide chemistry described here is a direct analogue to the hydrolytic sol–gel chemistry of tetraalkylorthosilicates for the preparation of silica gels, and represents the first example of ammonolytic sol–gel synthesis of a porous silicon diimide gel. The chemistry of **1** is ammenable to the synthesis of other single-source molecular precursors for non-oxide gels, and in future papers we will report on the preparation of Si–Al, Si–B and Si–Ti compounds and imide gels derived from them.

Experimental Section

1: Anhydrous dimethylamine (45.3 g, 1.86 mol) was allowed to react with silicon tetrachloride (45 g, 0.27 mol) in diethyl ether (1.5 L) at −40 °C over 15 h. The resulting dimethylammonium chloride was removed by filtration and washed with diethyl ether (2 × 200 mL). The combined solutions of $[(CH_3)_2N]_3SiCl$ in diethyl ether were cooled to −50 °C, and anhydrous liquid ammonia (70 g, 4.0 mol) was added in two aliquots. After 15 h the precipitated ammonium chloride was removed by filtration at room temperature, and the filtrate concentrated under reduced pressure to provide **1** as a colorless liquid (99.2% purity according to GC/MS). Yield 35.1 g (0.20 mol, 74% based on $SiCl_4$); b.p. 186 °C (760 torr); elemental analysis calcd: C 40.9, H 11.4, N 31.8, Si 15.9; found: C 40.8, H 10.9, N 31.8, Si 15.8; ^1H NMR (300 MHz, C_6D_6): $\delta = 2.3$ (s, 18H, $Si[N(CH_3)_2]_3$), 0.3 (brs, 2H, $SiNH_2$); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 37.89$ (s, $Si[N(CH_3)_2]_3$); ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -21.73$ (s, $Si[N(CH_3]_2)_3$); ^{15}N NMR (60.8 MHz, C_6D_6, external CH_3NO_2): $\delta = -376.1$ (NH_2), −375.4 ($N(CH_3)_2$); IR (liquid film): $\tilde{\nu} = 3475$ (w), 3406 (w; 2 × $\nu(NH_2)$), 2972 (s), 2835 (s), 2788 (s; 3 × $\nu(CH_3)$), 1552 cm^{-1} (m) ($\delta(NH_2)$); MS (EI): *m/z* (%): 176 (100) [M^+], 132 (90) [$M^+ - N(CH_3)_2$].

2. To a sample of **1** (2.5 g, 14.2 mmol) was added trifluoromethanesulfonic acid (12 μL, 0.142 mmol, 1 mol%) under argon, and the mixture heated to 100 °C, resulting in evolution of gaseous dimethylamine. After about 4 h the mixture was cooled to room temperature where it solidified to a colorless crystalline mass. Extraction into pentane (5 mL) and cooling to −80 °C gave colorless crystalline **2**. Yield 1.1 g (61%). Elemental analysis calcd: C 36.6, H 9.90, N 32.0, Si 21.3; found: C 36.9, H 9.86, N 32.0, Si 21.3; ^1H NMR (300 MHz, C_6D_6): $\delta = 2.43$ (s, 12H, $Si[N(CH_3)_2]_3$), 0.0 (brs, 3H, SiNH); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 36.61$ (s, $Si[N(CH_3)_2]_2$); ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -31.5$ (s, $Si[N(CH_3)_2]$; IR (KBr): $\tilde{\nu} = 3392$ (m), (ν(NH)), 2971 (s), 2865 (s, sh), 2855 (s, sh), 2834 (s), 2786 (s; 5 × ν(CH_3)), 1171 (s), 987 cm^{-1} (s); MS (EI): m/z (%): 393 (20) [M^+], 349 (20) [$M^+ - N(CH_3)_2$], 303 (100) [$M^+ - 2\,N(CH_3)_2$].

Crystal structure analysis of **2**: Crystals of **2** were grown from pentane at −40 °C, crystal dimensions 0.63 × 0.24 × 0.11 mm; $\lambda = 0.71073$ Å; crystallographic data at 100 K: triclinic, space group $P\bar{1}$ (no. 2); $a = 832.83(17)$, $b = 1069.0(2)$, $c = 1408.3(3)$ pm; $\alpha = 69.62(3)$, $\beta = 74.95(3)$, $\gamma = 69.41(3)^\circ$; $V = 1.0867(4)$ nm^3; $Z = 2$; $\rho_{calcd} = 1.203$ Mg m^{-3}; $F(000) = 432$; $\mu(Mo_{K\alpha}) = 0.234$ mm^{-1}. Data were collected on a Bruker AXS SMART-CCD-System with ω scans. Of 13 602 reflections collected ($4.24^\circ < 2\theta > 55.04^\circ$), 4891 were independent ($R_{int} = 0.0622$). The structure was solved by direct methods (SHELXS-97[22]) and refined by full-matrix least squares on F^2 using 241 parameters ($R(F) \geq 4\sigma(F) = 0.0470$, $wR2 = 0.1328$); max./min. residual electron density 0.728/ − 0.571 e Å^{-3}. Hydrogen atoms were located from the difference Fourier map, all methyl hydrogen atoms were constrained to idealized positions, and imido hydrogen atoms were refined freely. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112321. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Silicon imide gel preparation by ammonolysis of **1** and **2**: To a solution of **1** (2.5 g, 14.2 mmol) in dry THF (100 mL) in a 250-mL round-bottomed glass flask was added trifluoromethanesulfonic acid (12 μL, 0.14 mmol, 1 mol%). On warming to 50 °C evolution of gaseous dimethylamine was observed. After 18 h analysis by IR and MS showed complete conversion of **1** into **2** (ca. 80%) and other unidentified by-products (ca. 20%). A solution of ammonia (42 mmol) in dry THF (40 mL) was added, and the mixture was left quiescent at 50 °C for 18 h, at which point a slight opalescence was observed. Addition of further ammonia (14 mmol) resulted in rapid gelation to give, after several minutes, a translucent rigid gel filling the original volume of the reaction mixture. Evaporation of the solvent and dimethylamine in a stream of argon followed by drying under reduced pressure at 50 °C for 10 h yielded a translucent white solid. IR (KBr): $\tilde{\nu} = 3475$ (w, sh; (ν(NH_2)), 3362 (m; ν(NH)), 2973 (m), 2863 (m, sh), 2857 (m, sh), 2835 (m), 2787 (m; ν(CH_3)), 1551 (w; δ(NH_2)), 1181 (s), 985 cm^{-1} (s).

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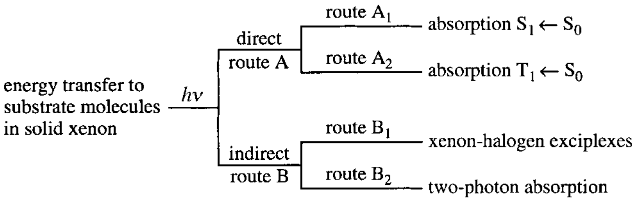
Solid Xenon: A Medium for Unusual Photoreactions[**]

Günther Maier[*] and Christian Lautz

As is shown in this communication, a molecule isolated in a xenon matrix at 10 K can react upon irradiation depending on the conditions by four, in principle different mechanisms (Scheme 1). Of course, as in any other transparent medium a substance absorbing in the wavelength region of the irradiating light can be induced to undergo a photoreaction also in a xenon matrix ($S_1 \leftarrow S_0$ absorption; direct route A_1). For instance, matrix irradiation ($\lambda = 313$ nm) of 2-diazo-2*H*-imidazole in argon as well as in xenon leads to 2*H*-imidazol-2-ylidene.[1] In this case the special feature of xenon lies only in its ability to stabilize the generated carbene by complexation.[1]



Scheme 1. Possible photoexcitations of a substrate molecule in a xenon matrix.

Surprisingly, in a xenon matrix even those molecules are accessible for photoreactions, which cannot absorb light at the wavelength employed. This phenomenon can be observed when the xenon matrix is doped with halogen atoms (indirect route B_1).[2] Hereby the halogen atoms absorb the excitation energy, which is stored in xenon halogen exciplexes, whose

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[*] Prof. Dr. G. Maier, Dipl.-Chem. C. Lautz
Institut für Organische Chemie der Universität
Heinrich-Buff-Ring 58, D-35392 Giessen (Germany)
Fax: (+49) 641-99-34309

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