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Syntheses and structures of $[(Me_3N)_3SiNHLi]_4$, $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$, $((Me_2N)_3SiNH)_3Al$ and $Li(THF)_2{}^+[((Me_2N)_3SiNH)_4Al]^-$

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The preparation of lithium tris(dimethylamino)silylamide, $[(Me_3N)_3SiNHLi]_4$, **2**, and its reaction with aluminium trichloride to give tris(dimethylamino)silylamino)(tetrahydrofuran)alane, $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$, **3**, and bis(tetrahydrofuran)lithium tetrakis(tris(dimethylamino)silylamino)alanate, $Li(THF)_2{}^+[((Me_2N)_3SiNH)_4Al]^-$, **6**, is reported, together with the crystal structures of **2**, **3** and **6**. Tris(dimethylamino)alane, $((Me_2N)_3SiNH)_3Al$, was obtained by reaction of tris(dimethylamino)silylamine with aluminium triethyl. The ammonolytic gelation of **3** to an imidoaluminosilicate gel is also described.

Introduction

The chemistry of compounds in which a main-group element is bound to a maximum number of nitrogen atoms is under scrutiny as a potential source of precursor molecules for the chemical synthesis of nitride-based inorganic materials. We recently reported a method for the preparation, by a non-aqueous, ammonolytic sol–gel technique, of a high surface area porous silicon diimide gel by the acid catalyzed ammonolysis of tris(dimethylamino)silylamine, $(Me_2N)_3SiNH_2$, TDSA, **1**, thus establishing an imide analog to the hydrolytic sol–gel chemistry of orthosilicate esters to form silica gels.[1] This chemistry has two immediate areas of impact. First, since silicon diimide is a precursor for high purity silicon nitride,[2] this sol–gel method leading to imidosilicate gels provides a potentially important method for the preparation and processing of ceramics based on silicon nitride, and similarly for nitridosilicate solids.[3] Secondly there is current interest in the preparation of micro- and mesoporous non-oxide solids analogous to the wide range of porous oxide materials. Materials in this form are now recognised as offering technological opportunities beyond their traditional uses as adsorbents and catalysts and catalyst supports,[4] and as the ammonolytic sol–gel method produces high surface area porous imidosilicate solids, we anticipate its extensive use in this application.

This chemistry has a further related application to the preparative chemistry of crystalline multinary nitridosilicates,[5,6] recently reviewed by Schnick and Huppertz[3] These important materials, which are the nitride analogs to the oxosilicates which dominate the inorganic chemistry of silicon, are prepared by solid state synthesis techniques at high temperature, for example by the reaction between metal powders and silicon diimide under r.f. heating.[7] The high temperatures used in these preparations are necessary to overcome the slow diffusion rates of atoms in the solid particles of reactants and products. As a general synthetic strategy these diffusion rates are increased by use of high reaction temperatures (1000–1500 °C), and thus, as a consequence of the high temperatures involved, only the most thermodynamically stable products are obtained. The use of bimetallic imidosilicate gels as starting materials in which the metal atoms are already dispersed at atomic level should allow a wider range of crystalline multinary nitridosilicates to be prepared, at lower temperatures.

The co-ammonolysis of mixtures of metalalkylamides has recently been reported as a route to multinary silicon-based nitride ceramics.[8] We are following an analogous sol–gel route to these important materials but using as starting materials presynthesised multinary silylamides. The chemistry of **1** is particularly ammenable to the preparation of a wide range of such compounds. The synthetic strategy we have adopted is to assemble precursor molecules containing, in addition to peripheral $Si(NMe_2)_3$ groups, an $M(NHSiN_3)_n$ core. In such compounds each of the ceramogenic metal centres is in an exclusively MN_4 environment. By these means we expect to be able to use the proven ammonolytic susceptibility[1] of the $Si(NMe_2)_3$ periphery of the molecule to develop ternary imidosilicate gels in which M and Si atoms are interdispersed on the atomic level, thus extending the ammonolytic sol–gel method to the preparation of multinary nitride ceramics.

The compounds whose syntheses and structures we report here were designed as a means to allow us to explore further the use of single source precursors for the preparation *via* ammonolytic sol–gel chemistry of imidometalosilicates (nitrogen analogues to oxidic metalosilicates), and, from them, of metal nitridosilicates. Given the extensive chemistry of aluminosilicates in oxide chemistry, we chose imidoaluminosilicates as our first target system. As has been recognized by Roesky and coworkers[9] such nitrogen analogues to aluminosilicates were unknown until 1997.

We report here the use of **1** *via* its lithium salt, lithium tris(dimethylamino)silylamide, $[(Me_2N)_3SiNHLi]_4$, **2**, as a reagent for the preparation of two new imidoaluminosilicates, tris(tris(dimethylamino)silylamino)alane as its THF adduct, $(THF)Al(NH(Si(NMe_2)_3)_3$, **3**. THF-free tris(tris(dimethylamino)silylamino)alane, $Al(NH(Si(NMe_2)_3)_3$, **4**, was also prepared by the protolysis reaction of **1** with triethylaluminium. Dilithio(tetrakis(tris(dimethylamino)silylamino))alanate, as its bis-THF adduct, $[(THF)_2Li]^+[((Me_2N)_3SiNH)_4Al]^-$, **6**, was prepared by reaction of **2** with anhydrous aluminium trichloride in the appropriate molar ratios. The X-ray crystal structures of **2**, for which we anticipate extensive application in the synthesis of silylamide compounds, of **3** and of **6** are reported. In the context of their potential as precursors for carbon-free imidosilicate gels none of these compounds contain Si–C or Al–C bonds, and each of the ceramogenic elements Si and Al are in exclusively MN_n environment. We show also that **3** and **4**

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are useful precursors for the preparation of imidoaluminosilicate gels.

Results and discussion

Lithium tris(dimethylamino)silylamide, $[(Me_2N)_3SiNHLi]_4$, 2

Compound **1**, prepared from dimethylamine, silicon tetrachloride and ammonia,[1] reacted with one equivalent of *n*-butyllithium in mixed pentane–hexane solution at 0 °C with evolution of one equivalent of butane. The product, **2**, was isolated in quantitative yield by crystallization at −80 °C from the reaction mixture as a white, air-sensitive solid, and was characterized by ^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR and FTIR spectroscopy. The IR spectrum of the crystalline solid showed clearly the disappearance of the two characteristic absorptions at 3420 and 3390 cm^{-1} due to the symmetric and asymmetric NH stretching modes of the $SiNH_2$ group in **1**. A new band at 3354 cm^{-1} was assigned to the ν(NH) stretching mode of a SiNHLi group, consistent with lithiation of the amino group of **1**. The ^{1}H NMR confirms the occurrence of the deprotonation reaction and comprises two signals, the first at 2.50 ppm, assigned to the $Si(NMe_2)_3$ (18H), and a second at −1.70 ppm assigned to the Si–NHLi proton (1H) in the appropriate ratio for **2** (for **1**, only one resonance is seen for the methyl protons at 2.46 ppm, while the Si–NH protons are found at 0.31 ppm). The ^{13}C NMR shows only one resonance at 39.28 ppm. The ^{15}N spectrum shows two resonances, the first at −373 ppm assigned to the NMe_2 nitrogen (−374 ppm in **1**), and the second at −364 ppm, assigned to the Si–NHLi nitrogen.

Crystals of **2** suitable for X-ray diffraction were grown from pentane solution at −80 °C. The structure of **2** is shown in Fig. 1.

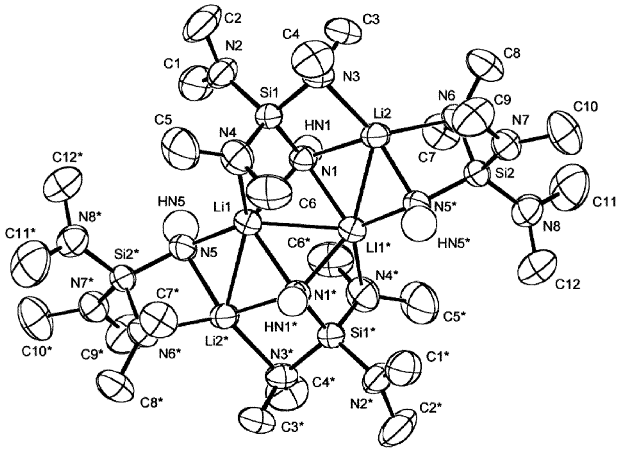


Fig. 1 ORTEP[10] plot of the molecular structure of compound **2**. Hydrogen atoms in the dimethylamino groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)–N(1) 1.674(2), Si(1)–N(2) 1.704(3), Si(1)–N(3) 1.763(2), Si(1)–N(4) 1.722(3), Li(1)–N(5) 2.007(5), Li(1)–N(1) 2.058(5), Li(1)–N(4) 2.619(5), Li(1)–N(5)* 1.980(5); N(1)–Si(1)–N(4) 106.3, N(2)–Si(1)–N(1) 115.7, N(3)–Si(1)–N(1) 107.5, N(3)–Si(1)–N(2) 108.3, N(1)*–Li(1)–N(5) 104.9, N(1)*–Li(1)–N(1) 105.2, N(5)–Li(1)–N(4) 122.6, N(5)–Li(1)–N(1) 135.2, N(1)*–Li(1)–N(4) 116.2. Equivalent positions are generated by the symmetry operator: $-x$, $-y+z$, $-z$.

The molecule possesses a crystallographic inversion centre, and comprises a central Li_2N_2 ring which shares two opposite Li–N edges with two further Li_2N_2 rings forming a four-rung ladder. All three Li_2N_2 rings are planar, and the dihedral angles between the central ring and the outer rings are 135.5 ± 0.5°. Condensed ladder structures such as this are often found in lithium amide chemistry when the lithium cation is complexed by a Lewis base.[11] Uncomplexed lithium amides commonly comprise $(LiN)_x$ rings condensed in extensive amorphous structures, but complexation of the cation allows small condensed ring molecules to be isolated. Examples of this are the TMEDA and PMDETA complexes of pyrrrolidinyl lithium[12] in which three Li_2N_2 rings form a condensed four-rung ladder as is the case for **2**. In **2** the necessary complexing agent, which coordinates to the terminal lithium atoms, is the additional functionality provided by the dimethylamino group of one of the tris(dimethylamino)silylamido groups, and thus **2** is a self-terminating ladder structure.

The ^{1}H and ^{13}C NMR spectra of **2** require comment since as can be seen from Fig. 1, several environments are distinguishable for the dimethylamino methyl groups. At the lowest level of differentiation the dimethyamino groups are either associated with a lithium cation or are free, and the observation of only a single resonance in the ^{13}C and ^{1}H spectra implies an exchange of these environments in solution which is rapid on the NMR time scale.

Tris(dimethylaminosilylamino)(tetrahydrofuran)alane, 3

The reaction of **2** with aluminium trichloride in THF under mild conditions results, after addition of pentane, in the precipitation of a quantitative amount of lithium chloride and the formation of **3** in high yield. IR and NMR spectroscopy were consistent with the formulation of **3** as tris(dimethylaminosilylamino)(tetrahydrofuran)alane, $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$. The IR spectrum exhibited bands at 3335 cm^{-1} (ν(NH)) and 1555 cm^{-1} (δ(NH)) in addition to absorptions attributable to (ν(CH)) at 2980, 2835 and 2769 cm^{-1}. The ^{1}H NMR spectrum exhibited a singlet at 2.27 ppm and a low intensity broad resonance at 0.00 ppm ascribable to SiNMe and SiNHAl groups respectively. In addition a triplet at 3.90 and a quintet at 1.33 ppm due to THF were observed. ^{13}C NMR showed three resonances which are assigned to the dimethylamino groups (38.58 ppm) and to THF (69.12 and 25.10 ppm), respectively. The ^{29}Si NMR spectrum contained only one singlet at −31.65 ppm. All attempts to obtain acceptable elemental analyses for **3** were unsuccessful. Mass spectrometry was also unsuccessful, resulting in the facile displacement of THF from **3** and subsequent decomposition.

Crystals of **3** suitable for X-ray diffraction were grown from pentane solution at −80 °C. The appearance of the crystals suggested some decomposition had occurred prior to attempting data collection. This may be due to loss of THF from the crystal sample and resulted in a lower quality data set, however a satisfactory refinement was achieved

The molecular structure of **3** is shown in Fig. 2. The central aluminium atom in **3** is bonded to three tris(dimethylamino)silylamino groups. The molecule contains an approximately tetrahedral $AlON_3$ core but with considerable variation among the three Al–N bonds (1.722(4), 1.774(4) and 1.817(4) Å. The angles subtended at the central Al atom by each of the three nitrogen atoms and the THF oxygen atom varied from 97.00(15) to 119.00(19)°. The geometry of the $AlON_3$ core of **3** reflects the larger steric bulk of the tris(dimethylamino)silylamino groups in comparison to THF.

Tris(tris(dimethylamino)silylamino)alane, $Al(NH(Si(NMe_2)_3)_3$, 4

Attempts to prepare a THF-free form of **3** by reaction of **2** with $AlCl_3$ in pentane were unsuccessful, resulting only in low yields of $Li^+[((Me_2N)_3SiNH)_4Al]^-$, (see **5** and **6** below). An alternative approach, taking advantage of the weak acidity of the NH_2 protons in **1** was more fruitful. When three equivalents of **1** in toluene were allowed to react with one equivalent of aluminium triethyl, added dropwise as toluene solution, at 50 °C, the protolysis reaction shown in eqn. (1) occurs smoothly over a period of 24 h and affords a quantitative yield of ethane (measured volumetrically) and, on evaporation of the toluene, the new silylamidoalane $Al[NHSi(NMe_2)_3]_3$, **4**, as a viscous oil.

All attempts to crystallise **4** were unsuccessful, and the compound was characterised solely by IR, NMR, cryoscopic

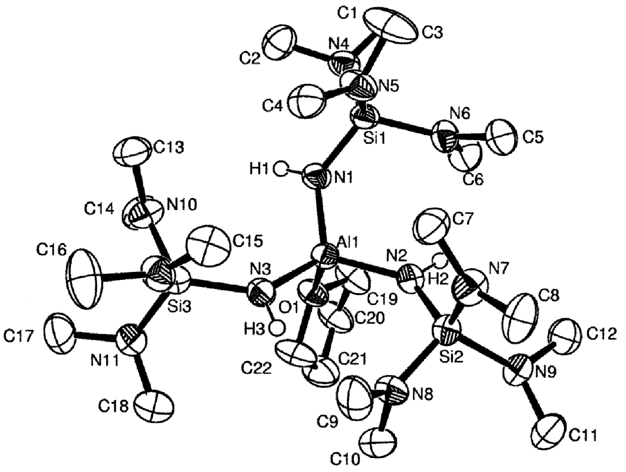
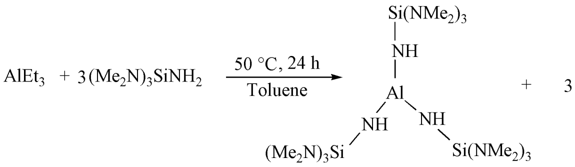


Fig. 2 ORTEP[10] plot of the molecular structure of compound **3**. Hydrogen atoms in the dimethylamino groups and THF are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.722(4), Al(1)–N(2) 1.817(4), Al(1)–N(3) 1.774(4), Al(1)–O(1) 1.877(3), Si(1)–N(1) 1.583(4), Si(2)–N(2) 1.689(4), Si(3)–N(3) 1.689(4); N(1)–Al(1)–N(3) 119.00(19), N(1)–Al(1)–N(2) 114.11(18), N(3)–Al(1)–N(2) 113.84(17), N(1)–Al(1)–O(1) 97.00(15), N(3)–Al(1)–O(1) 104.86(16), N(2)–Al(1)–O(1) 104.82(16), Si(1)–N(1)–Al(1) 129.1(2), Si(2)–N(2)–Al(1) 133.3(2), Si(3)–N(3)–Al(1) 137.7(4).



$$AlEt_3 + 3(Me_2N)_3SiNH_2 \xrightarrow[\text{Toluene}]{50\ °C,\ 24\ h} Al(NHSi(NMe_2)_3)_3 + 3\ EtH \quad (1)$$

molecular weight determination and elemental analysis. The comparison between the IR spectra of the starting silylamine **1** and the product **4** shows the disappearance of the two $\nu(NH_2)$ bands at 3450 and 3400 cm^{-1}, characteristic of **1**, and the appearance of a new absorbance at 3330 cm^{-1}, assigned to the Al–NH–Si linkage. Mass spectroscopic analysis was not possible for **4**, owing to decomposition during the measurement liberating **1** and dimethylamine, probably through self-condensation reactions. The molecular weight of **4** was measured cryoscopically in benzene, and showed it to be monomeric in solution (measured 548, calculated for **4** 552). The ^{1}H NMR and ^{13}C NMR spectra contain only singlets, at 2.8 ppm and 41 ppm, respectively, evidence for the presence of a single type of dimethylaminosilylamide group, while resonances corresponding to the NH protons were not observed.

These data allow the formulation of **4** as monomeric tris(tris(dimethylamino)silylamino)alane, $Al(NH(Si(NMe_2)_3)_3$. This is one of very few examples of non-spirocyclic triamidoalanes. These include the sterically hindered dialkylaminoalanes, such as $Al(NMe_2)_3$,[13] $Al(NEt_2)_3$,[14] $Al(NPr^i_2)_3$,[15] and $Al[N(SiMe_3)_2]_3$.[16] Moreover there is only one example reported of a trisubstituted *primary* amidoalane $Al((NHPh)_3$.[17] An intriguing cage imidoaluminosilicate was reported by Roesky and coworkers from the reaction of the sterically hindered triaminosilane $RSi(NH_2)_3$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$NSiMe$_3$) with trimethylaluminium, in a reaction analogous to that which we have used here.[18]

Bis(tetrahydrofuranato)dilithio(tetrakistris(dimethylamino)-silylamino)alanate, $[(THF)_2Li^+]_2[((Me_2N)_3SiNH)_4Al]^-$, 6

The isolation of low yield of an anionic tetrakis(silylamido)-alanate in the attempted synthesis of **4** from $AlCl_3$ and **2** in pentane in a 3 : 1 molar ratio prompted us to prepare this compound in high yield by reaction of **2** with $AlCl_3$ in a 4 : 1 ratio. The reaction proceeded smoothly in pentane at 20 °C with the precipitation of 3.0 equivalents of lithium chloride (eqn. (2)). Filtration and evaporation of the solvent gave an colorless oily product identified by elemental analysis, FTIR and NMR spectroscopy as $Li^+[((Me_2N)_3SiNH)_4Al]^-$, **5**. Addition of two equivalents of THF to a pentane solution of this product and cooling to −80 °C yielded the white crystalline THF adduct $Li(THF)_2{}^+[((Me_2N)_3SiNH)_4Al]^-$, **6**. Crystals of **6** suitable for X-ray diffraction were grown from pentane–THF solution at −80 °C. The structure of **6** is shown in Fig. 3. The molecule possesses crystallographic C_2 symmetry, with the central aluminium atom bound to four tris(dimethylamino)-silylamino nitrogen atoms in a distorted tetrahedral fashion. The two Al–N(1) distances involving imido nitrogen atoms which are also coordinated to the lithium cation are slightly longer (1.893 Å) than the remaining two Al–N(2) distances (1.842 Å). The N(1)–Al–N(1)* angle in the four-membered AlN_2Li ring is more acute (102.8(1)°) than the N(2)–Al–N(2)* angles (119.1(1)°).

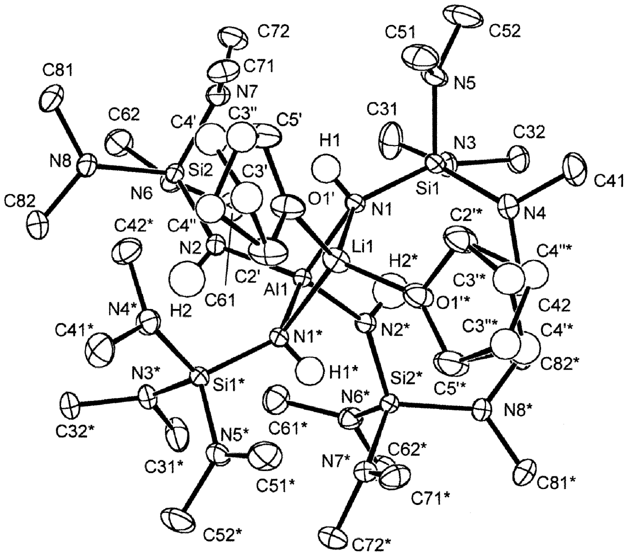


Fig. 3 ORTEP[10] plot of the molecular structure of compound **6**. Hydrogen atoms in the dimethylamino groups and THF are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.893(2), Al(1)–N(2) 1.842(2), Si(1)–N(1) 1.718(1), Si(2)–N(2) 1.694(1), Li(1)–N(1) 2.139(3), Li(1)–O(1′) 2.003(2); N(1)*–Al(1)–N(1) 1.028, N(2)*–Al(1)–N(2) 119.1, Al(1)–N(1)–Li(1) 84.8, N(1)*–Li(1)–N(1) 87.5, O(1′)*–Li(1)–O(1′) 95.0. Equivalent positions are generated by the symmetry operator: $-x + 2, y, -z + 1/2$.

$$4(Me_2N)_3SiNHLi + AlCl_3 \xrightarrow[\text{Pentane}]{20\ °C,\ 24\ h} [Li]^-[Al(NHSi(NMe_2)_3)_4]^+ + 3\,LiCl \quad (2)$$

Compound **6** shows the same structural features as the previously reported aluminium amide $(Et_2O)_2Li^+[Al(NMe_2)_4]^-$,[19,20] in which the aluminium is in a tetrahedral coordination environment, as is the lithium cation which is coordinated to two diethylether molecules as external ligands and to two dimethylamine nitrogen atoms. Compound **6** is nevertheless the first structurally characterized molecular compound containing an aluminium bound to four *primary* amide groups, suggesting that the silylamide anion $[(Me_2N)_3SiNH]^-$, due to its steric dimensions, is particularly effective in stabilising otherwise labile classes of metal imide molecules.

Ammonolysis and gelation of 3 and 4

Having demonstrated previously the facile ammonolysis of TDSA to give silicon diimide gels,[1,21] we anticipated the reaction of ammonia with these new ternary imidosilicates would yield ternary imide gels.

On treating a solution of **3** in dry terahydrofuran with a cooled (−80 °C) solution of ammonia in dry THF in the presence of a catalytic quantity of trifluoromethanesulfonic acid at room temperature for 18 h followed by 72 h at 50 °C, a translucent gel formed filling about half of the original volume of the reaction mixture. Decantation of the solution above the gel and evaporation of the remaining solvent and the dimethylamine produced in the gelation process by a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a translucent white solid. The IR spectrum of this gel is shown in Fig. 4. In addition to the broad ν(N–H) band at 3350–3450 cm^{-1}, ν(N–C) at 1176 cm^{-1} and ν(Si–N) at 920 cm^{-1}, there is a broad band at 712 cm^{-1} which can be ascribed to ν(Al–N).[22] The low intensity of ν(CH) bands from 2790 to 2973 cm^{-1} indicates that most of the dimethylamino groups in compound **3** (Fig. 4(a)) have been removed. Both ^{29}Si CP-MAS NMR and ^{27}Al CP-MAS NMR showed only single resonances at −40 ppm and 120 ppm, respectively, corresponding to the presence of Si[N$_4$] and AlN$_4$ species.[23,24] ^{13}C CP-MAS NMR showed only one broad resonance at 38 ppm ascribed to residual dimethylamino groups, and no resonances due to THF were observed. These results suggest that ammonolysis of **3** produced a silicon aluminium imide gel containing residual dimethylamino groups, and that the THF in compound **3** has been removed during the gelation. The gel exhibits a mesoporous structure (type IV physisorption isotherm), with an average pore diameter of 3.7 nm and a BET surface area of 528 m^2 g^{-1}.

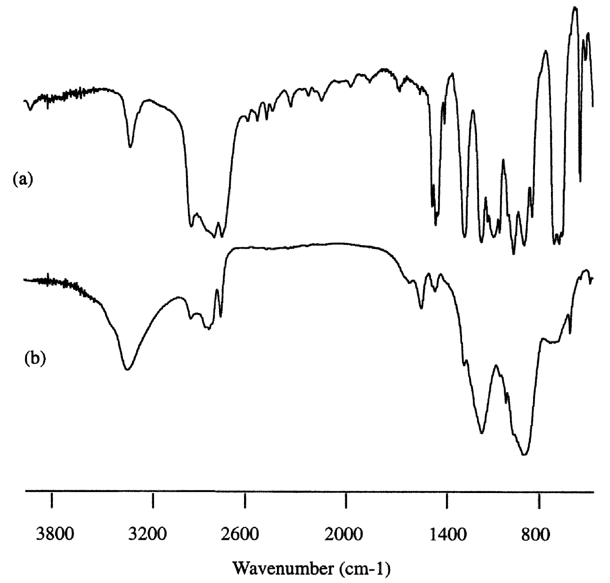


Fig. 4 IR spectra of (a) (THF)Al[NHSi(NMe$_2$)$_3$]$_3$, **3** and (b) the gel from **3**; (a) and (b) were recorded by neat and KBr plate technique, rspectively

A similar procedure using **4** as the gel precursor resulted in a transparent gel after only 24 h, which after separation, washing with THF and drying was shown to be homogeneous by EDAX analysis (5 nm probe size). FTIR showed the presence of residual dimethylamino groups at a similar level to the gel derived from **3**, which could be removed by further treatment with ammonia, yielding an aluminoimidosilicate gel with a surface area of 310 m^2 g^{-1} and a broad pore size distribution in the mesopore range.

Summary

Two novel tris(tris(dimethylamino)silylamino)alanes: (THF)Al(NH(Si(NMe$_2$)$_3$)$_3$, **3** and Al(NH(Si(NMe$_2$)$_3$)$_3$, **4** were prepared by reaction of tris(dimethylamino)silylamidolithium, **2** with aluminium chloride and tris(dimethylamino)silylamine, **1** with aluminium triethyl, respectively. Dilithio(tetrakis(tris(dimethylamino)silylamino))alanate, [Li]$^+$[((Me$_2$N)$_3$SiNH)$_4$Al]$^-$, **5**, and its bis-THF adduct, [(THF)$_2$Li]$^+$[((Me$_2$N)$_3$SiNH)$_4$Al]$^-$, **6** were obtained when **2** was reacted with aluminium chloride in 4 : 1 molar ratio. It has been shown that **1** is a good starting material for the synthesis of NH bridged imidosilicates based on the acidity of its SiNH$_2$ protons.

High surface area aluminoimidosilicate gels were successfully prepared from the catalytic ammonolysis of **3** and **4** in dry THF, thus extending the chemistry of **1** to the preparation of multinary silicon based imide gels. The synthesis of a variety of bimetallic silylamides derived from **1**, and their uses as sources of imidosilicate gels for the preparation of ternary nitride ceramics are under active investigation.

Experimental

General procedures

All the procedures were performeded under protective nitrogen atmosphere using standard Schlenk techniques or a nitrogen-filled glove box. Silicon tetrachloride, dimethylamine and ammonia were purchased from Fluka and used as received. Aluminium trichloride was purchased from Aldrich and purified by sublimation. Trifluoromethansulfonic acid, *n*-butyllithium (1.6 M in hexane) and aluminium triethyl were purchased from Aldrich and used as received. Solvents were dried and distilled under dry nitrogen by the usual methods.

High-resolution NMR spectra were obtained on a JEOL JNM-LA400FT NMR spectrometer using C$_6$D$_6$ as solvent. IR spectra were recorded on a Nicolet Magna-500 FTIR spectrometer. MS spectra were obtained by fractional distillation of the sample on Finnigan MAT 8200 and 8400 spectrometers. Elemental analyses were performed by Kolbe Microanalitiches Labor (Mülheim an der ruhr, Germany). ^{29}Si and ^{13}C CP-MAS NMR were recorded on a Bruker DSX-300 spectrometer operating at frequencies of 59.6 and 75.5 MHz, respectively. ^{27}Al was measured at frequency of 78.1 MHz with a single pulse sequence. Nitrogen adsorption isotherms were performed at 77 K using a Micrometritics ASAP 2010 instrument, and surface area was determined from BET analysis.

Syntheses

(Me$_2$N)$_3$SiNH$_2$, 1. **1** was prepared from silicon tetrachloride, dimethylamine and ammonia by a modification of the previously reported method.[1] Anhydrous dimethylamine (127 mL, 85.1 g, 1.90 mol) was condensed at −50 °C into a graduated glass trap, and then passed under dry nitrogen into a solution of silcon tetrachloride (47.2 g, 0.28 mol) in diethyl ether (1.5 L) at −40 °C. The resulting suspension was stirred for 15 h during which time the mixture had reached room temperature) (*ca.* 20 °C). The resulting dimethylammonium chloride was removed by filtration and washed with diethyl ether (2 × 200 mL). The combined ether solutions of (Me$_2$N)$_3$SiCl were cooled to −50 °C and excess anhydrous liquid ammonia (64 g, 4.3 mol) was added in two aliquots. After stirring for 15 h the precipitated ammonium chloride was removed by filtration at room temperature, and the filtrate concentrated under reduced pressure leaving a colourless liquid residue of tris(dimethylamino)silylamine (Me$_2$N)$_3$SiNH$_2$ (99.2% purity by GC/MS). Yield 35.1 g (0,20 mol; 74% based on SiCl$_4$) bp 186 °C (760 Torr). The product was distilled at 60 °C/0.1 Torr and stored under dry nitrogen. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 2.5 (s, 18H, Si(N(CH$_3$)$_2$)$_3$, 0.31 (w, 2H, NH$_2$Si); ^{13}C NMR (400 MHz, C$_6$D$_6$): δ 37.88 (SiN(CH$_3$)$_2$); ^{29}Si NMR: δ −33.78 ppm; IR (cm^{-1}): 3474 (w), 3405 (w) (ν(NH$_2$)); 1553 (m) (δ(NH)).

[(Me$_2$N)$_3$SiNHLi]$_4$, 2. To a rapidly stirred solution of **1** (3.8 g, 21.6 mmol) in pentane (150 mL) at 0 °C was added *n*-butyllithium (13.4 mL, 1.6 M, 1.0 equivalents) under argon. Gas evolution was observed, and after stirring at 0 °C for 6 h the solution was cooled to −80 °C for 18 h. The resulting white crystalline solid, **3**, was isolated by decantation and washing with cold (–80 °C) pentane. Yield 2.9 g (16.4 mmol, 76%). Evaporation of the combined decantate and washings followed by crystallisation from pentane at −80 °C yielded a further 0.9 g of **3** (5.2 mmol, 24%). Calc. for $C_{24}H_{76}N_{16}Si_4Li_4$: C, 39.5; H, 10.5; N, 30.7; Li, 3.81; Si, 15.4. Found: C, 39.5; H, 10.4; N, 30.7; Li, 3.74; Si, 15.3%. ^{1}H NMR (600 MHz, C_5D_{12}): δ 2.50 (s, 18H, NCH_3), −1.70 (s, 1H, NH); ^{13}C NMR (75 MHz, C_5D_{12}): δ 39.28 (NCH_3); ^{29}Si NMR (79.5 MHz, C_5D_{12}): δ −21.5; ^{15}N NMR (60.8 MHz, C_5D_{12}, *vs.* external CH_3NO_2): δ −364 (NH), −373 ($N(CH_3)_2$); IR (KBr, cm^{-1}): 3449 (m) (ν(NH)); 2949 (s), 2910 (s), 2846 (s), 2813 (s) ($\nu(CH_3)$); 1549 (w); 1483 (m), 1465 (m) (δ(NH)); 995 (s) (ν(SiN)).

A crystal of $[(Me_2N)_3SiNHLi]_4$ suitable for X-ray diffraction experiment was transferred under argon into a Pypex capillary, which was then sealed *in vacuo* and collected on Enraf-Nonius CAD4 Vierkreis. The structure was solved by direct methods (SHELXS-86)[25] and refined against F^2 (SHELXL-97).[26]

$(C_4H_8O)Al[NHSi(NMe_2)_3]_3$, 3. A solution of 5.89 g (32.4 mmol) LiTDSA in 50 mL THF was added to a solution of 1.45 g (10.9 mmol) $AlCl_3$ in 50 mL THF at 0 °C. After 30 min, the reaction mixture was returned to room temperature and stirred for about 10 h. After THF was exchanged by same volume of pentane, the resulting precipitate of lithium chloride was removed by filtration, and the filtrate was evaporated under reduced pressure to give a slightly yellow oil. The oil was dissolved in 25 mL pentane and cooled to −80 °C for three days giving white crystals. After separating from pentane by decantation and washing twice with cooled (*ca.* −80 °C) pentane, the crystals were dried under reduced precursor. Yield (5.49 g, 8.77 mmol, 80 %). ^{1}H NMR: δ 2.72 (s, 54 H, NCH_3), 3.90 (t, 4 H, CH_2O), 1.33 (qnt, 4 H, $CH_2CH_2CH_2$); ^{13}C NMR: δ 38.58 (NCH_3), 69.12 (CH_2O), 25.10 ($CH_2CH_2CH_2$). ^{29}Si NMR: δ −31.65. IR (neat, cm^{-1}): 3335 (m) (ν(NH)); 2980 (s), 2835 (s), 2769 (s) (ν(CH)); 1555 (m) (δ(NH)); 1170 (s); 992 (s).

A crystals of $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$, suitable for single crystal X-ray crystallography, was coated with an Perfluoropolyether PFO-XR75 oil under a constant nitrogen flow. The crystal with oil coating was rapidly transferred to the goniometer head at 150 K and data collected on a STOE IPDS II diffractometer. The structure was solved by direct methods (SHELXS-86)[25] and refined against F^2 (SHELXL-97).[26] Data was collected to θ = 35°, however the poor crystal quality due to partial decomposition prior to data collection gave a high number of weak reflections and a high value of R_{int}. The structure was refined against truncated data sets with θ = 22.5, 25 or 30° for comparison and the solution presented with θ = 30°.

Preparation of gel from 3. To a solution of **3** (4.1 g, 6.5 mmol) in dry terahydrofuran (205 mL) was added trifluoromethanesulfonic acid (40 uL, 0.45 mmol). After stirring for 30 min, a cooled (*ca.* −80 °C) solution of ammonia (100 mmol) in dry THF (9 mL) was added. After standing quiescent at room temperature for 18 h, the mixture was warmed to 50 °C for 72 h, to give a translucent gel filling about half of the original volume of the reaction mixture. Decantation of the solution above the gel and evaporation of remaining solvent and dimethylamine in the gel by a stream of nitrogen followed by drying under reduced pressure at 50 °C for 6 h yielded a translucent white solid. ^{29}Si CP-MRS NMR: δ −40 ppm; ^{27}Al CP-MRS NMR: δ 120 ppm; ^{13}C CP-MRS NMR: δ 38 ppm; IR (KBr, cm^{-1}): 3355 (m) ((ν(NH)); 2973 (w), 2861 (w), 2776 (w) (ν(CH)); 1564 (w) (δ(NH)); 1176 (s) (δ(N–C)); 920 (s) (ν(Si–N)); 715 (w) (ν(Al–N)).

$Al(NHSi(NMe_2)_3)_3$, 4. $(Me_2N)_3SiNH_2$ (5.1 g, 29 mmol) diluted in 20 mL of toluene was added dropwise into 50 mL into a toluene solution of $AlEt_3$ (1.05 g, 9.2 mmol; Si : Al ratio 1 : 3) at 50 °C. The reaction mixture was then stirred for 24 h at 50 °C. Overall 581 mL of gas, identified by MS as ethane, were evolved as measure by a gas burette (calculated 618 mL, 94% of the theoretical value). The solvent was then removed under reduced pressure, and a pale yellow oil was obtained. Calc. for $C_{18}H_{57}N_{12}Si_9Al_3$: C, 39.1; H, 10.3; N, 30.4; Si, 14.7; Al, 4.88. Found: C, 38.6; H, 9.8; N, 30.9; Si, 15.2; Al, 5.00%; Si/Al = 2.92; MW (cryoscopy in benzene) 548 (calculated for $Al[NHSi(NMe_2)_3]_3$ 553). ^{1}H NMR (300 MHz, C_6D_6): δ 2.84 (s, NCH_2); ^{13}C NMR (300 MHz, C_6D_6): δ 41 (s, NCH_2); IR (KBr, cm^{-1}): 3330 (w) (ν(NH)); 2972 (s), 2831 (s), 2783 (s) (ν(CH)); 1541 (w) (δ(NH)); 984(s) (ν(SiN)).

$Li[Al(NHSi(NMe_2)_3]_4$, 5. To a rapidly stirred suspension of $AlCl_3$ (250 mg, 1.9 mmol) in pentane (10 mL) was added dropwise at room temperature a solution of $(Me_2N)_3SiNHLi$, **2**, (1.36 g, 7.5 mmol) in pentane (15 mL). The reaction mixture was stirred for 18 h. The resulting precipitate of lithium chloride was removed by filtration, and the filtrate was evaporated under reduced pressure to give a colourless oil, characterised as $Li[Al(NHSi(NMe_2)_3]_4$, **5**, (1.29 g, 94% based on $AlCl_3$). Calc. for $C_{24}H_{76}N_{16}LiSi_4Al_4$: C, 39.0; H, 10.4; N, 30.3; Si, 15.7. Found: C, 39.1; H, 10.2; N, 30.4; Si, 15.5%. ^{1}H NMR (600 MHz, C_7D_8): δ 2.61 (s, 72H, $Si(N(CH_3)_2)_3$), 0.05 (br s, 4H, SiNH); ^{13}C NMR (75 MHz, C_7D_8): δ 38.8 (s, $SiN((CH_3)_2)_3$); ^{29}Si NMR (279.5 MHz, C_6D_6): δ −30.2 $Si(N(CH_3)_2)_3$); ^{15}N NMR (60.8 MHz, C_7D_8, *vs.* external CH_3NO_2): δ −358.4 (NH), −373.0 ($N(CH_3)_2$); IR (liquid film, cm^{-1}): 3327 (m) (ν(NH)); 2974 (s), 2839 (s), 2783 (s) ($\nu(CH_3)$); 1551 (m) (δ(NH)); 1182 (s) (ν(SiN)); 986 (s).

The bis(tetrahydrofuran) adduct of **5**, **6**, was crystallised from solutions of **5** by addition of 2.0 equivalents of THF and cooling to −80 °C. A crystal of **6** suitable for X-ray diffraction was transferred under argon into a Pypex capillary, which was then sealed *in vacuo* and data collected on Siemens SMART CCD diffractometer. The structure was solved by direct methods (SHELXS-86)[25] and refined against F^2 (SHELXL-97).[26]

Crystallographic data

Crystal structure determination of compound **2** $[(Me_2N)_3SiNHLi]_4$: $C_{24}H_{76}Li_4N_{16}Si_4$; M = 729.13; monoclinic, space group $P2_1/n$; a = 11.5670(5), b = 8.9071(8), c = 22.3754(16) Å; α = 90, β = 96.861(5), γ = 90°; V = 2288.8(3) Å^3; T = 293 K; Z = 2; D_c = 1.058 Mg m^{-3}; μ(Mo-Kα) = 0.165 mm^{-1}; F(000) = 800; 5345 reflections collected, 5217 independent (R_{int} = 0.0159) used in refinement. $R1$ = 0.0487 on $F > 4\sigma(F)$, $wR2$ = 0.181 on all data.

Crystal structure determination of compound **3** $(C_4H_8O)Al[NHSi(NMe_2)_3]_3$: $C_{22}H_{65}AlN_{12}OSi_3$; M = 625.11; monoclinic, space group $P2_1/c$; a = 9.7875(16), b = 17.413(2), c = 21.810(4) Å; α = 90, β = 112.536(14), γ = 90° V = 3433.2(9) Å^3; T = 150 K; Z = 4; D_c = 1.209 Mg m^{-3}; μ(Mo-Kα) = 0.200 mm^{-1}; F(000) = 1376, 29973 reflections collected, 10569 independent (R_{int} = 0.2043) used in refinement. $R1$ = 0.0716 on $F > 4\sigma(F)$, $wR2$ = 0.1620 on all data.

Crystal structure determination of compound **6** $Li(THF)_2^+$-$[((Me_2N)_3SiNH)_4Al]^-$: $C_{32}H_{92}AlLiN_{16}O_2Si_4$; M = 879.50; monoclinic, space group $C2/c$ (no. 15); a = 12.2318(4), b = 21.7844(9), c = 20.2211(6) Å; α = 90, β = 105.3130(10), γ = 90°; V = 5196.9(3) Å^3; T = 100 K; Z = 4; D_c = 1.124 Mg m^{-3}; μ(Mo-Kα) = 0.350 mm^{-1}; F(000) = 1936, 27683 reflections collected, 9089 independent (R_{int} = 0.0294) used in refinement. $R1$ = 0.0407 on $F > 4\sigma(F)$, $wR2$ = 0.118 on all data.

CCDC reference numbers 172029, 194606 and 194607.

See http://www.rsc.org/suppdata/dt/b2/b209605f/ for crystallographic data in CIF or other electronic format.

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