

# Syntheses and structural studies of lithium complexes of 2-amino-6-methylpyridine †

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Lithiation of 2-amino-6-methylpyridine (C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub>) occurred smoothly in diethyl ether (OEt<sub>2</sub>) or hexane–N,N,N',N'-tetramethylethylenediamine (tmeda) affording [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(OEt<sub>2</sub>)<sub>0.5</sub>] **1** or [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(tmeda)] **2**. These complexes are extremely moisture sensitive and rapidly yield [Li<sub>8</sub>(C<sub>5</sub>H<sub>3</sub>NMeNH)<sub>6</sub>(O)(OEt<sub>2</sub>)<sub>2</sub>] **3** and [Li<sub>8</sub>(C<sub>5</sub>H<sub>3</sub>NMeNH)<sub>6</sub>(O)(tmeda)<sub>2</sub>] **4** respectively, upon exposure to limited amounts of water. On treatment of **1** with dimethylsilicone, insertion of dimethylsilicone into the Li–N bond occurs affording [Li<sub>4</sub>(C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>2</sub>O)<sub>4</sub>] **5**. All complexes were characterised by spectroscopic and X-ray crystallographic methods. Complexes **3** and **4** reveal octanuclear centrosymmetric structures with an octahedral oxygen centre bound by six lithium atoms, and in **4** a *monodentate* tmeda ligand is identified. Compound **5** is tetranuclear with an Li<sub>4</sub>O<sub>4</sub> pseudo-cubane core with each of these lithium atoms involved in six-membered chelate rings comprised of N–C–N–Si–O atoms with the lithium bound to the terminal N and O heteroatoms.

## Introduction

Interest in lithium complexes has gained considerable attention, and those of anionic N-centred species (lithium amides) are no exception,<sup>1</sup> mainly because of their fundamental importance as synthetic reagents in inorganic chemistry and as strong Bronsted bases or nucleophiles in organic synthesis.<sup>2</sup> The structures of these complexes, both in the solid state and solution, is of great importance, since they can significantly affect the outcome of syntheses or transformations. Association in the solid state can be expected due to the high polarity of the Li–N bond,<sup>3</sup> unless sterically hindered ligands are employed.<sup>4</sup> It is widely recognised that, due to the ease of hydrolysis of organolithium complexes according to  $RLi + H_2O \rightarrow RH + LiOH$ , all handling of these reagents must be under the strict exclusion of moisture using Schlenk and/or glove box techniques under an inert atmosphere. However, the nature of the material obtained by the *controlled* addition of water to lithium reagents has attracted little attention. Furthermore, the interaction between organolithium reagents and organosilicone reagents ([R<sub>2</sub>SiO]<sub>n</sub>) has one precedent, *viz.* our recent publication of a lithium complex of 8-aminoquinoline.<sup>5</sup>

In this paper we report the synthesis, reactivity and structural studies of some N-functionalised amidolithium compounds based on 2-amino-6-methylpyridine (C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub>). This work is related to that we have previously published on the substantially more sterically hindered 2-methyl-6-(trimethylsilylamino)pyridine (C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>3</sub>) system where a number of organoamide complexes have been synthesized,<sup>6</sup> as well as some studies of some 8-aminoquinoline.<sup>7</sup> It was of initial interest to us to determine how the degree of nuclearity changes in the absence of the bulky trimethylsilyl group and to develop this reagent as a transfer reagent in the synthesis of further organoamide complexes. For lithium reagents of C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>3</sub>, centrosymmetric dimers dominate, for

example the etherate and tetrahydrofuranate [Li(C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>3</sub>)(L)]<sub>2</sub> (L = Et<sub>2</sub>O<sup>6a</sup> or thf<sup>8</sup>) while the tetramethylethylenediamine adduct is monomeric, [Li(C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>3</sub>)(tmeda)].<sup>6a</sup> In the absence of SiMe<sub>3</sub> groups higher aggregates can be expected due to the much lower steric hindrance.

Several reports on the reactivity of lithium reagents with controlled amounts of water have identified a common structural motif. In these systems a central Li<sub>2</sub>O molecule becomes entrapped by additional lithium alkyl, amido or phosphide complexes creating cluster molecules such as {Li<sub>2</sub>[C(R<sup>1</sup>)SO<sub>2</sub>R<sup>2</sup>]}<sub>6</sub>·Li<sub>2</sub>O·10thf (R<sup>1</sup> = SiMe<sub>3</sub>, R<sup>2</sup> = Ph),<sup>9</sup> [Li<sub>2</sub>(salen)]<sub>3</sub>·Li<sub>2</sub>O·2tmeda·H<sub>2</sub>O (H<sub>2</sub>salen = N,N'-bis(salicylidene)ethane-1,2-diamine,<sup>10</sup> [Li<sub>14</sub>{(c-C<sub>5</sub>H<sub>6</sub>)N(H)}<sub>12</sub>(O)]<sub>11</sub> and [Li<sub>18</sub>(tPr<sub>2</sub>(Mes)-SiP)<sub>8</sub>O] (Mes = 2,4,6-trimethylphenyl)<sup>12</sup> where a central Li<sub>6</sub>O core is repeatedly found. This sixfold co-ordination of O<sup>2-</sup> by metal ions in molecular compounds is rare and has only been identified in the previous mentioned complexes and in a mixed lithium–barium *tert*-butoxide–oxide aggregate.<sup>13</sup>

Recently, there has been interest in the reaction of organometallic and organoamide complexes with dimethylsilicone polymers. The general reaction involves the insertion of Me<sub>2</sub>SiO into the Ln–N bond, *e.g.* in the pyrazolate complexes [Yb(C<sub>5</sub>H<sub>4</sub>Me)(pzMe<sub>2</sub>)(OSiMe<sub>2</sub>pzMe<sub>2</sub>)<sub>2</sub>]<sub>14</sub> (HpzMe<sub>2</sub> = 3,5-dimethylpyrazole) and [LnCp(pzMe<sub>2</sub>)(OSiMe<sub>2</sub>pzMe<sub>2</sub>)<sub>2</sub>] (Ln = Dy or Ho).<sup>15</sup> Furthermore, TIOEt is known to react with dimethylsilicone polymer, generating [Ti<sub>2</sub>(OSiMe<sub>2</sub>)<sub>2</sub>O]<sub>n</sub>.<sup>16</sup> No analogous lithium amides undergoing such reactions have been reported.

Herein we report the synthesis of some lithiated 2-amino-6-methylpyridine complexes and their reaction with water creating unusual OLi<sub>6</sub> cluster complexes and also a reaction with dimethylsilicone where insertion of SiMe<sub>2</sub>O into the Li–N bond occurs.

## Experimental

2-Amino-6-methylpyridine and n-BuLi (1.6 mol dm<sup>-3</sup> solu-

† This paper is dedicated to Professor Colin Raston on the occasion of his 50th birthday.

tion in hexane) were purchased from Aldrich and used as received. 2-Methyl-6-(trimethylsilylamino)pyridine was prepared according to the literature procedure.<sup>6a</sup> Diethyl ether and thf were dried over CaH<sub>2</sub> then freshly distilled from sodium-benzophenone and all manipulations were performed using conventional Schlenk or glove-box techniques under an atmosphere of high-purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls in sodium chloride plates on a Perkin-Elmer 1600 series FTIR spectrophotometer, <sup>1</sup>H NMR spectra at 300.13 MHz using a Bruker BZH 300/52 spectrometer with a Varian console; chemical shifts were referenced against solvent. The compounds obtained in this study were too air/moisture sensitive to obtain reasonable elemental analyses.

### Preparations

**[Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(Et<sub>2</sub>O)<sub>0.5</sub>], 1.** n-Butyllithium (2.90 cm<sup>3</sup>, 1.6 mol dm<sup>-3</sup> in hexane, 4.64 mmol) was added to a solution of C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub> (0.5 g, 4.64 mmol) in diethyl ether (≈20 cm<sup>3</sup>) at 0 °C, and stirred at room temperature for 30 minutes. The volatiles were then removed *in vacuo* and the minimum volume of diethyl ether was added, resulting in a colourless powder. Yield 90%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>H<sub>6</sub>): δ 6.92 (t, 2 H, N<sub>(amido)</sub>-H), 5.88 (d, 2 H, H<sup>2</sup> arom.), 5.85 (d, 2 H, H<sup>3</sup> arom.), 3.60 (s, 2 H, N-H), 3.21 (t, 8 H, CH<sub>2</sub> ether), 1.90 (s, 6 H, C<sub>arom</sub>-CH<sub>3</sub>) and 1.05 (s, 12 H, CH<sub>3</sub> ether). IR (Nujol, ν): 3677s, 1600m, 1557s, 1238s, 1085s and 781s cm<sup>-1</sup>.

**[Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(tmeda)], 2.** n-Butyllithium (9.25 cm<sup>3</sup>, 1.6 mol dm<sup>-3</sup> in hexane, 14.81 mmol) was added slowly to a solution of C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub> (1.6 g, 14.81 mmol) in hexane (≈20 cm<sup>3</sup>) at 0 °C, and stirred at room temperature for 30 minutes. tmeda (2.25 cm<sup>3</sup>, 14.81 mmol) was then added at room temperature. Yield 92%. The volatiles were removed *in vacuo*. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.92 (t, 1 H, H<sup>1</sup> arom.), 5.89 (d, 1 H, H<sup>2</sup> arom.), 5.86 (d, 1 H, H<sup>3</sup> arom.), 3.38 (s, 1 H, N-H), 2.22 (s, 3 H, C<sub>arom</sub>-CH<sub>3</sub>), 2.00 (s, 4 H, N-CH<sub>2</sub>) and 1.98 (s, 12 H, N-CH<sub>3</sub>). IR (Nujol, ν): 3401s, 1609s, 1260s, 1096m, 1023m and 801s cm<sup>-1</sup>.

**[Li<sub>8</sub>(C<sub>5</sub>H<sub>3</sub>NMeNH)<sub>6</sub>(O)(OEt<sub>2</sub>)<sub>2</sub>], 3.** [C<sub>5</sub>H<sub>3</sub>NMeNHLi] (6.02 mmol) in diethyl ether (≈20 cm<sup>3</sup>) was treated with distilled water (0.014 cm<sup>3</sup>, 0.75 mmol) at 0 °C. The solution was stirred for 10 minutes before the volatiles were removed *in vacuo* and the minimum volume of diethyl ether was added. Yield 45%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.32 (t, 6 H, H<sup>1</sup> arom.), 6.52 (d, 6 H, H<sup>2</sup> arom.), 6.32 (d, 6 H, H<sup>3</sup> arom.), 4.33 (s, 6 H, N-H), 3.61 (q, 8 H, CH<sub>2</sub> ether), 2.37 (s, 18 H, C<sub>arom</sub>-CH<sub>3</sub>) and 1.22 (t, 12 H, CH<sub>3</sub> ether). IR (Nujol, ν): 3401s, 1601m, 1077s and 776s cm<sup>-1</sup>.

**[Li<sub>8</sub>(C<sub>5</sub>H<sub>3</sub>NMeNH)<sub>6</sub>(O)(tmeda)<sub>2</sub>], 4.** n-Butyllithium (9.25 cm<sup>3</sup>, 1.6 mol dm<sup>-3</sup> in hexane, 14.81 mmol) was added slowly to a solution of C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub> (1.6 g, 14.81 mmol) in hexane (≈20 cm<sup>3</sup>) at 0 °C, and stirred at room temperature for 30 minutes. tmeda (2.25 cm<sup>3</sup>, 14.81 mmol) was added at room temperature, followed by distilled water (0.033 cm<sup>3</sup>, 1.85 mmol) at 0 °C. The volatiles were then removed *in vacuo* and the minimum volume of hexane-tmeda was added at -30 °C. Yield 54%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.91 (t, 6 H, H<sup>1</sup> arom.), 6.19 (d, 6 H, H<sup>2</sup> arom.), 5.68 (d, 6 H, H<sup>3</sup> arom.), 4.33 (s, 6 H, N-H), 2.53 (s, 18 H, C<sub>arom</sub>-CH<sub>3</sub>), 2.31 (s, 8 H, N-CH<sub>2</sub>) and 2.08 (s, 24 H, N-CH<sub>3</sub>). IR (Nujol, ν): 3401s, 1609s, 1260s, 1096m, 1023m and 801s cm<sup>-1</sup>.

**[Li<sub>4</sub>(C<sub>5</sub>H<sub>3</sub>NMeNHSiMe<sub>2</sub>O)<sub>4</sub>], 5.** [C<sub>5</sub>H<sub>3</sub>NMeNHLi] (3.98 mmol) in diethyl ether (20 cm<sup>3</sup>) was treated with dimethylsilicone (0.12 g, 3.98 mmol) at 0 °C. The solution was allowed to stir for 30 minutes before the volatiles were removed *in vacuo* and the minimum volume of diethyl ether was added. Long colourless needle crystals resulted. Yield 60%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.95 (t, H<sup>1</sup> arom.), 6.23 (d, H<sup>2</sup> arom.), 5.76 (d, H<sup>3</sup>

arom.), 3.72 (s, N-H), 2.29 (s, C<sub>arom</sub>-CH<sub>3</sub>) and 1.32 (s, Si-Me<sub>2</sub>). IR (Nujol, ν): 3406m, 1609m, 1573s, 1246s, 1013m and 777s cm<sup>-1</sup>.

### Collection of X-ray diffraction data, and solution and refinement of the structures

For compound **3** a data set was acquired on an Enraf-Nonius CAD4 diffractometer for capillary mounted specimens. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*,*y*,*z*, *U*<sub>iso</sub>)<sub>H</sub> were included constrained at estimated values. The structure was refined using the XTAL 3.4 program system implemented by S. R. Hall.<sup>17</sup> The crystal decomposed slightly during data collection (approx. 20%). For **4** and **5** hemispheres of data were collected on a Bruker SMART CCD diffractometer and corrected for absorption using the program SADABS.<sup>18</sup> The structures were solved using direct methods (SHELXS)<sup>19</sup> and refined on *F*<sup>2</sup> using SHELXL 97-2.<sup>20</sup> All non-hydrogen atoms were located and refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions (riding model) and not refined.

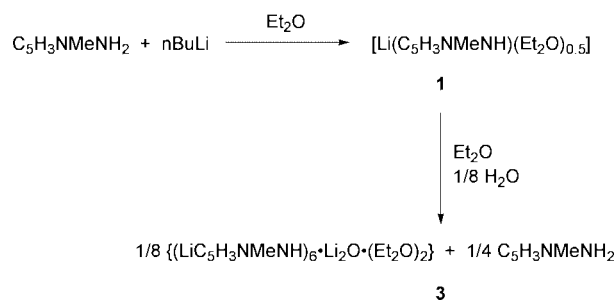
Crystal data and a summary of data collection appear in Table 1 and pertinent results are shown in Tables 2–4 and the Figures.

CCDC reference number 186/2096.

See <http://www.rsc.org/suppdata/dt/b0/b004322m/> for crystallographic files in .cif format.

### Discussion

Lithiation of 2-amino-6-methylpyridine (C<sub>5</sub>H<sub>3</sub>NMeNH<sub>2</sub>) with one equivalent of nBuLi in diethyl ether at 0 °C rapidly formed a colourless solution containing [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(Et<sub>2</sub>O)<sub>0.5</sub>] **1** (Scheme 1). All attempts to crystallise this complex failed,



Scheme 1

resulting in a colourless powder of unknown degree of aggregation, but the stoichiometry of the complex (after drying *in vacuo* at ca. 60 °C) was obtained by NMR spectroscopy. The <sup>1</sup>H NMR spectrum displays a resonance for the N-H protons at δ 3.60, which is upfield of that of the “free” ligand (δ 5.15). Resonances occur between δ 5.85 and 6.92 for the aromatic protons. The resonances for the co-ordinated diethyl ether protons occur at δ 1.90 and 3.21 which are slightly shifted from those for free diethyl ether (δ 1.1 and 3.5). The ν(N-H) stretching frequency is evident in the infrared spectrum at 3677 cm<sup>-1</sup>. Lithiation of 2-amino-6-methylpyridine with one equivalent of n-BuLi in hexane-tmeda yielded a colourless solution from which colourless [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(tmeda)] **2** (Scheme 2) was isolated after removal of the solvent *in vacuo*. For compound **2** the <sup>1</sup>H NMR spectrum confirmed the 1:1 ratio of ligand to tmeda and has resonances at δ 6.92 to 5.86, 3.38, and 2.22 due to the aromatic, N-H and the C<sub>arom</sub>-CH<sub>3</sub> protons respectively, and at δ 2.00 and 1.98 due to the CH<sub>2</sub> and CH<sub>3</sub> protons on the tmeda ligand respectively. The ν(N-H) stretch in the infrared was readily identifiable at 3401 cm<sup>-1</sup>.

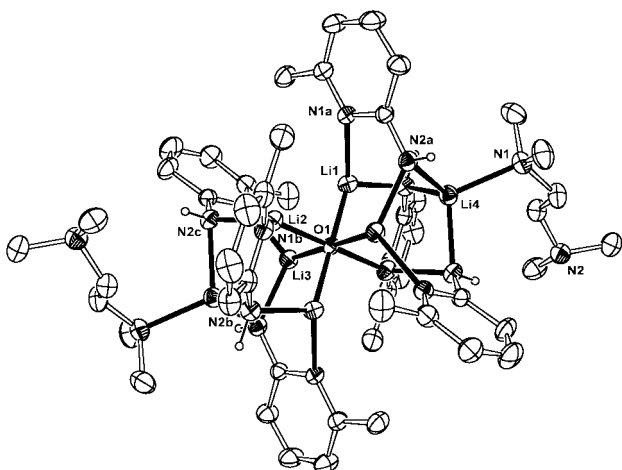
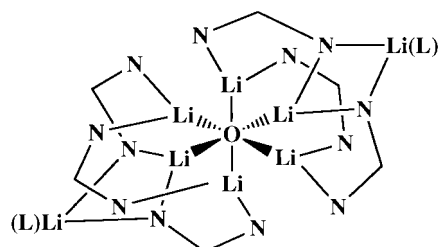
While we were unable to obtain crystals of [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(Et<sub>2</sub>O)<sub>*n*</sub>] **1** or [Li(C<sub>5</sub>H<sub>3</sub>NMeNH)(tmeda)<sub>*n*</sub>] **2** it was possible



**Table 3** Selected bond distances (Å) and angles (°) for  $[\text{Li}_8(\text{C}_5\text{H}_3\text{NMeNH})_6(\text{O})(\text{tmeda})_2]_4$ 

Li(1)–O(1)	1.866(5)	Li(3)–O(1)	1.867(4)
Li(1)–N(1A)	2.001(5)	Li(3)–N(2A)#1	2.008(5)
Li(1)–N(2B)#1	2.018(5)	Li(3)–N(1C)	2.030(5)
Li(2)–O(1)	1.881(5)	Li(4)–N(2C)#1	2.070(5)
Li(2)–N(1B)	1.999(5)	Li(4)–N(2A)	2.090(5)
Li(2)–N(2C)	2.001(5)	Li(4)–N(2B)#1	2.115(5)
Li(4)–N(1)#2	2.120(5)		
O(1)–Li(1)–N(1A)	126.6(2)	O(1)–Li(3)–N(1C)	120.1(2)
O(1)–Li(1)–N(2B)#1	114.7(2)	O(1)–Li(3)–N(2A)#1	114.9(2)
N(1A)–Li(1)–N(2B)#1	108.7(2)	N(1C)–Li(3)–N(2A)#1	114.4(2)
O(1)–Li(2)–N(1B)	121.0(2)	N(2A)–Li(4)–N(1)#2	108.6(2)
O(1)–Li(2)–N(2C)	116.4(2)	N(2A)–Li(4)–N(2B)#1	107.6(2)
N(1B)–Li(2)–N(2C)	115.8(2)	N(2B)#1–Li(4)–N(1)#2	115.6(2)
N(2C)#1–Li(4)–N(1)#2	110.8(2)	N(2C)#1–Li(4)–N(2A)	109.0(2)
N(2C)#1–Li(4)–N(2B)#1	105.0(2)	Li(2)–O(1)–Li(2)#1	180.0
Li(1)–O(1)–Li(1)#1	180.0	Li(2)–O(1)–Li(3)	87.2(2)
Li(1)–O(1)–Li(2)	94.5(2)	Li(3)–O(1)–Li(3)#1	180.0
Li(1)–O(1)–Li(3)	92.0(2)		

Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, -y, -z$ ; #2  $-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$ .

**Fig. 2** Molecular structure of  $[\text{Li}_8(\text{C}_5\text{H}_3\text{NMeNH})_6(\text{O})(\text{tmeda})_2]_4$ , with an octahedral central oxygen and a “dangling” tmeda ligand.

3 L = Et<sub>2</sub>O  
4 L = η<sup>1</sup>-tmeda

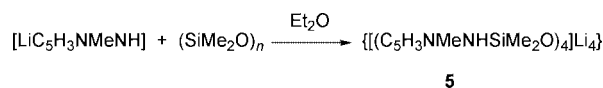
$[\text{Li}_8(\text{C}_5\text{H}_3\text{NMeNH})_6(\text{O})(\text{tmeda})_2]_4$  were isolated (Fig. 2, Table 3). The overall structure of compound **4** is similar to that of **3** where a central  $\text{OLi}_6$  fragment is observed. In place of the co-ordinated Et<sub>2</sub>O solvent in compound **3** a ‘dangling’ monodentate tmeda is bound to the lithium centre with the Li–N distance of 2.120(5) Å. To our knowledge this is only the second observation of this type of binding in organolithium chemistry, and curiously the only other incidence of this binding mode was observed in a complex with an  $\text{OLi}_6$  core as a feature in its structural motif, viz.  $[\text{Li}_2(\text{salen})_3]_3 \cdot \text{Li}_2\text{O} \cdot 2\text{tmeda} \cdot \text{H}_2\text{O}$ .<sup>10</sup> As in **3**, the ligands do not act as chelating agents to the lithium centres. The Li–N(arom.) distances average 2.01 Å and the Li–N(amido) distances on the same ligand average 2.633 Å, whereas the Li–N(amido) distances to an adjacent ligand average 2.009 Å exemplifying a bridging rather than chelate mode of binding. In other lithium complexes of 2-

**Table 4** Selected bond distances (Å) and angles (°) for  $[\text{Li}_4(\text{C}_5\text{H}_3\text{NMeNHSiMe}_2\text{O})_4]_5$ 

Li(1)–O(1B)	1.92(1)	Li(2)–O(1C)	1.938(9)
Li(1)–O(1A)	1.968(9)	Li(2)–O(1A)	1.952(9)
Li(1)–O(1D)	1.977(9)	Li(2)–O(1B)	1.961(9)
Li(1)–N(1A)	2.07(1)	Li(2)–N(1B)	2.146(9)
Li(3)–O(1B)	1.917(9)	Li(4)–O(1C)	1.911(9)
Li(3)–O(1D)	1.971(9)	Li(4)–O(1A)	1.912(9)
Li(3)–O(1C)	1.988(9)	Li(4)–O(1D)	2.009(8)
Li(3)–N(1C)	2.10(1)	Li(4)–N(1D)	2.087(9)
O(1A)–Li(1)–O(1B)	99.3(4)	O(1B)–Li(3)–O(1C)	99.1(4)
O(1A)–Li(1)–O(1D)	98.0(4)	O(1B)–Li(3)–O(1D)	97.3(4)
O(1B)–Li(1)–O(1D)	97.0(4)	O(1C)–Li(3)–O(1D)	96.8(4)
O(1A)–Li(1)–N(1A)	104.8(4)	O(1B)–Li(3)–N(1C)	112.7(5)
O(1B)–Li(1)–N(1A)	114.9(5)	O(1C)–Li(3)–N(1C)	102.2(4)
O(1D)–Li(1)–N(1A)	136.3(5)	O(1D)–Li(3)–N(1C)	140.9(4)
O(1A)–Li(2)–O(1C)	95.5(4)	O(1A)–Li(4)–O(1C)	97.7(4)
O(1A)–Li(2)–O(1B)	98.4(4)	O(1A)–Li(4)–O(1D)	98.8(4)
O(1B)–Li(2)–O(1C)	99.3(4)	O(1C)–Li(4)–O(1D)	98.1(4)
O(1A)–Li(2)–N(1B)	145.7(5)	O(1A)–Li(4)–N(1D)	138.7(5)
O(1B)–Li(2)–N(1B)	101.3(4)	O(1C)–Li(4)–N(1D)	113.8(4)
O(1C)–Li(2)–N(1B)	108.6(4)	O(1D)–Li(4)–N(1D)	102.3(4)

amino-6-methylpyridine<sup>6a</sup> the ligand acts as a chelating agent, except in a cluster complex where there are silylated and unsilylated ligands and seven unique lithium atoms. All Li–O–Li angles about the central core are close to 90° as with compound **3**.

In some related chemistry of lithiated aminoquinolines we were intrigued to identify a reaction between the lithium amide and dimethylsilicone, which yielded a novel tetranuclear species.<sup>5</sup> We were therefore prompted to follow some similar chemistry with the 2-amino-6-methylpyridine analogue and to study the effect of the smaller chelate in comparison with 8-aminoquinoline. During a synthesis of compound **1** a second crystal morphology and colour was observed. A crystal structure determination revealed the complex as  $[\text{Li}_4(\text{C}_5\text{H}_3\text{NMeNH-SiMe}_2\text{O})_4]_5$ . In a deliberate synthesis of **5**, dimethylsilicone was added to a diethyl ether solution of compound **1** resulting in a light straw-coloured solution (Scheme 3), which upon concen-

**Scheme 3**

tration and cooling, gave large colourless crystals of **5**. Compound **5** crystallises in the triclinic space group  $P\bar{1}$  with one whole molecule as the asymmetric unit (Fig. 3, Table 4). The

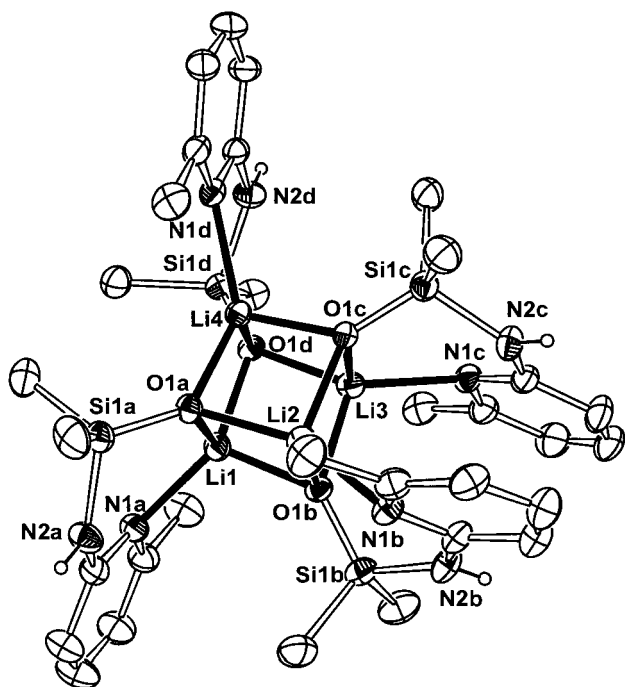
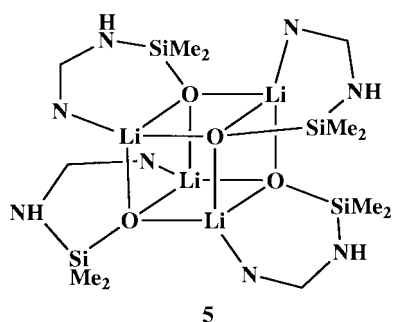


Fig. 3 Molecular structure of tetranuclear  $[\text{Li}_4(\text{C}_5\text{H}_3\text{NMeNHSiMe}_2\text{O})_4]^{5-}$ .



asymmetric unit consists of a tetranuclear aggregate comprised of four  $\text{C}_5\text{H}_3\text{NMeNHSiMe}_2\text{O}^-$  ligands and four lithium atoms with an  $\text{Li}_4\text{O}_4$  pseudo-cubane core as the main structural feature. In contrast to the chemistry we observed for the quinoline chemistry,<sup>5</sup> where insertion of  $\text{SiMe}_2\text{O}$  into the lithium–nitrogen bond occurred, followed by further reaction with the lithium amide, the present reaction terminated after insertion of dimethylsilicone into the Li–N bond. This is to our knowledge the second reported isolation of a compound with this type of dimethylsilicone insertion in lithium chemistry (the first being our work on 8-aminoquinoline),<sup>5</sup> although there have been reports of similar  $\text{SiMe}_2\text{O}$  insertions into  $\text{Ln-N}$  bonds ( $\text{Ln} = \text{Ho}, \text{Dy}$  or  $\text{Yb}$ ).<sup>14,15</sup> It is believed that the mechanism of this reaction proceeds *via* an intermediate where electropositive silicon is bound to the amido nitrogen and the lithium centre is bound to the O atom of the dimethylsilicone.<sup>14,15</sup> A related complex with an  $\text{Li}_4\text{O}_4$  cubane core has been observed from the treatment of  $t\text{Bu}_2\text{Si}(\text{NH}_2)\text{OH}$  with butyllithium yielding  $[\text{tBu}_2\text{Si}(\text{NH}_2)\text{OLi}]_4$ .<sup>21</sup> In the present  $\text{Li}_4\text{O}_4$  core the bond lengths and angles are very similar to those in  $[\text{tBu}_2\text{Si}(\text{NH}_2)\text{OLi}]_4$  (Li–Li, 2.52(1)–2.58(1); Li–O, 1.911(9)–2.009(8) Å; O–Li–O, 95.5(4)–99.3(4); Li–O–Li, 79.7(4)–83.3(4)).

## Conclusion

We have established some interesting structural chemistry and reactivity of nitrogen-functionalised lithium amides. Two novel

complexes containing the  $\text{OLi}_6$  core (with an octahedral oxygen atom) have been isolated. We also have shown that unprecedented dimethylsilicone insertion into a Li–N bond is possible upon treatment of a lithium amide with dimethylsilicone polymer.

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