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

Cameron Jones,[a] Peter C. Junk,*[b] Stuart G. Leary[b] and Neil A. Smithies[a]

[a] *Department of Chemistry, University of Wales, Cardiff, P.O. Box 912, Park Place, Cardiff, UK CF1 3TB*
[b] *Department of Chemistry, James Cook University, Townsville, Qld, 4811, Australia. E-mail: peter.junk@jcu.edu.au*

Lithiation of 2-amino-6-methylpyridine ($C_5H_3NMeNH_2$) occurred smoothly in diethyl ether (OEt_2) or hexane–N,N,N',N'-tetramethylethylenediamine (tmeda) affording $[Li(C_5H_3NMeNH)(OEt_2)_{0.5}]$ **1** or $[Li(C_5H_3NMeNH)(tmeda)]$ **2**. These complexes are extremely moisture sensitive and rapidly yield $[Li_8(C_5H_3NMeNH)_6(O)(OEt_2)_2]$ **3** and $[Li_8(C_5H_3NMeNH)_6(O)(tmeda)_2]$ **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 $[Li_4(C_5H_3NMeNHSiMe_2)_4]$ **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_4O_4 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,[1] mainly because of their fundamental importance as synthetic reagents in inorganic chemistry and as strong Brönsted bases or nucleophiles in organic synthesis.[2] 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,[3] unless sterically hindered ligands are employed.[4] It is widely recognised that, due to the ease of hydrolysis of organolithium complexes according to RLi + $H_2O \longrightarrow$ 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 ($[R_2SiO]_n$) has one precedent, *viz.* our recent publication of a lithium complex of 8-aminoquinoline.[5]

In this paper we report the synthesis, reactivity and structural studies of some N-functionalised amidolithium compounds based on 2-amino-6-methylpyridine ($C_5H_3NMeNH_2$). This work is related to that we have previously published on the substantially more sterically hindered 2-methyl-6-(trimethylsilylamino)pyridine ($C_5H_3NMeNHSiMe_3$) system where a number of organoamide complexes have been synthesized,[6] as well as some studies of some 8-aminoquinoline.[7] 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 $C_5H_3NMeNHSiMe_3$, centrosymmetric dimers dominate, for example the etherate and tetrahydrofuranate $[Li(C_5H_3NMe-NSiMe_3)(L)]_2$ (L = Et_2O[6a] or thf[8]) while the tetramethylethylenediamine adduct is monomeric, $[Li(C_5H_3NMeN-SiMe_3)(tmeda)]$.[6a] In the absence of $SiMe_3$ 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_2O molecule becomes entrapped by additional lithium alkyl, amido or phosphide complexes creating cluster molecules such as $\{Li_2[C(R^1)SO_2-R^2]\}_6\cdot Li_2O\cdot 10thf$ (R^1 = $SiMe_3$, R^2 = Ph),[9] $[Li_2(salen)]_3\cdot Li_2O\cdot 2tmeda\cdot H_2O$ (H_2salen = N,N'-bis(salicylidene)ethane-1,2-diamine,[10] $[Li_{14}\{(c-C_5H_9)N(H)\}_{12}(O)]$,[11] and $[Li_{18}(iPr_2(Mes)SiP)_8O]$ (Mes = 2,4,6-trimethylphenyl)[12] where a central Li_6O core is repeatedly found. This sixfold co-ordination of O^{2-} 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.[13]

Recently, there has been interest in the reaction of organometallic and organoamide complexes with dimethylsilicone polymers. The general reaction involves the insertion of Me_2SiO into the Ln–N bond, *e.g.* in the pyrazolate complexes $[Yb(C_5H_4Me)(pzMe_2)(OSiMe_2pzMe_2)]_2$[14] ($HpzMe_2$ = 3,5-dimethylpyrazole) and $[LnCp(pzMe_2)(OSiMe_2pzMe_2)]_2$ (Ln = Dy or Ho).[15] Furthermore, TlOEt is known to react with dimethylsilicone polymer, generating $[\{Tl_2(OSiMe_2)_2O\}]_n$.[16] 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_6 cluster complexes and also a reaction with dimethylsilicone where insertion of $SiMe_2O$ into the Li–N bond occurs.

Experimental

2-Amino-6-methylpyridine and n-BuLi (1.6 mol dm^{-3} solu-

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tion in hexane) were purchased from Aldrich and used as received. 2-Methyl-6-(trimethylsilylamino)pyridine was prepared according to the literature procedure.[6a] Diethyl ether and thf were dried over CaH_2 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, ^{1}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(C₅H₃NMeNH)(Et₂O)₀.₅], 1. n-Butyllithium (2.90 cm³, 1.6 mol dm⁻³ in hexane, 4.64 mmol) was added to a solution of $C_5H_3NMeNH_2$ (0.5 g, 4.64 mmol) in diethyl ether ($\approx$20 cm³) 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%. ^{1}H NMR (300 MHz, C_6H_6): δ 6.92 (t, 2 H, N_(amido)–H), 5.88 (d, 2 H, H² arom.), 5.85 (d, 2 H, H³ arom.), 3.60 (s, 2 H, N–H), 3.21 (t, 8 H, CH₂ ether), 1.90 (s, 6 H, C_arom–CH₃) and 1.05 (s, 12 H, CH₃ ether). IR (Nujol, v): 3677s, 1600m, 1557s, 1238s, 1085s and 781s cm⁻¹.

[Li(C₅H₃NMeNH)(tmeda)], 2. n-Butyllithium (9.25 cm³, 1.6 mol dm⁻³ in hexane, 14.81 mmol) was added slowly to a solution of $C_5H_3NMeNH_2$ (1.6 g, 14.81 mmol) in hexane ($\approx$20 cm³) at 0 °C, and stirred at room temperature for 30 minutes. tmeda (2.25 cm³, 14.81 mmol) was then added at room temperature. Yield 92%. The volatiles were removed *in vacuo*. ^{1}H NMR (300 MHz, C_6D_6): δ 6.92 (t, 1 H, H¹ arom.), 5.89 (d, 1 H, H² arom.), 5.86 (d, 1 H, H³ arom.), 3.38 (s, 1 H, N–H), 2.22 (s, 3 H, C_arom–CH₃), 2.00 (s, 4 H, N–CH₂) and 1.98 (s, 12 H, N–CH₃). IR (Nujol, v): 3401s, 1609s, 1260s, 1096m, 1023m and 801s cm⁻¹.

[Li₈(C₅H₃NMeNH)₆(O)(OEt₂)₂], 3. [C₅H₃NMeNHLi] (6.02 mmol) in diethyl ether ($\approx$20 cm³) was treated with distilled water (0.014 cm³, 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%. ^{1}H NMR (300 MHz, C_6D_6): δ 7.32 (t, 6 H, H¹ arom.), 6.52 (d, 6 H, H² arom.), 6.32 (d, 6 H, H³ arom.), 4.33 (s, 6 H, N–H), 3.61 (q, 8 H, CH₂ ether), 2.37 (s, 18 H, C_arom–CH₃) and 1.22 (t, 12 H, CH₃ ether). IR (Nujol, v): 3401s, 1601m, 1077s and 776s cm⁻¹.

[Li₈(C₅H₃NMeNH)₆(O)(tmeda)₂], 4. n-Butyllithium (9.25 cm³, 1.6 mol dm⁻³ in hexane, 14.81 mmol) was added slowly to a solution of $C_5H_3NMeNH_2$ (1.6 g, 14.81 mmol) in hexane ($\approx$20 cm³) at 0 °C, and stirred at room temperature for 30 minutes. tmeda (2.25 cm³, 14.81 mmol) was added at room temperature, followed by distilled water (0.033 cm³, 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%. ^{1}H NMR (300 MHz, C_6D_6): δ 6.91 (t, 6 H, H¹ arom.), 6.19 (d, 6 H, H² arom.), 5.68 (d, 6 H, H³ arom.), 4.33 (s, 6 H, N–H), 2.53 (s, 18 H, C_arom–CH₃), 2.31 (s, 8 H, N–CH₂) and 2.08 (s, 24 H, N–CH₃). IR (Nujol, v): 3401s, 1609s, 1260s, 1096m, 1023m and 801s cm⁻¹.

[Li₄(C₅H₃NMeNHSiMe₂O)₄], 5. [C₅H₃NMeNHLi] (3.98 mmol) in diethyl ether (20 cm³) 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%. ^{1}H NMR (300 MHz, C_6D_6): δ 6.95 (t, H¹ arom.), 6.23 (d, H² arom.), 5.76 (d, H³

arom.), 3.72 (s, N–H), 2.29 (s, C_arom–CH₃) and 1.32 (s, Si–Me₂). IR (Nujol, v): 3406m, 1609m, 1573s, 1246s, 1013m and 777s cm⁻¹.

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; $(x,y,z, U_{iso})_H$ were included constrained at estimated values. The structure was refined using the XTAL 3.4 program system implemented by S. R. Hall.[17] 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.[18] The structures were solved using direct methods (SHELXS)[19] and refined on F^2 using SHELXL 97-2.[20] 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.
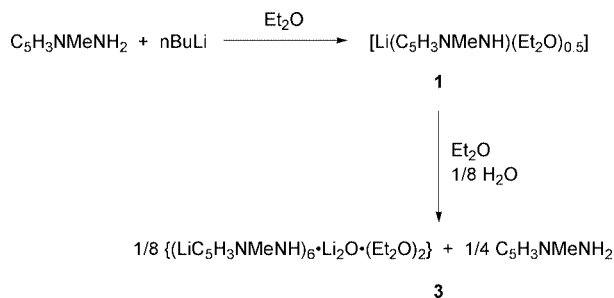
Crystal data and a summary of data collection appear in Table 1 and pertinent results are shown in Tables 2–4 and the Figures.

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 ($C_5H_3NMeNH_2$) with one equivalent of nBuLi in diethyl ether at 0 °C rapidly formed a colourless solution containing [Li(C₅H₃NMeNH)(Et₂O)₀.₅] **1** (Scheme 1). All attempts to crystallise this complex failed,

C₅H₃NMeNH₂ + nBuLi $\xrightarrow{\text{Et}_2\text{O}}$ [Li(C₅H₃NMeNH)(Et₂O)₀.₅]

1

Et₂O
1/8 H₂O

1/8 {(LiC₅H₃NMeNH)₆·Li₂O·(Et₂O)₂} + 1/4 C₅H₃NMeNH₂
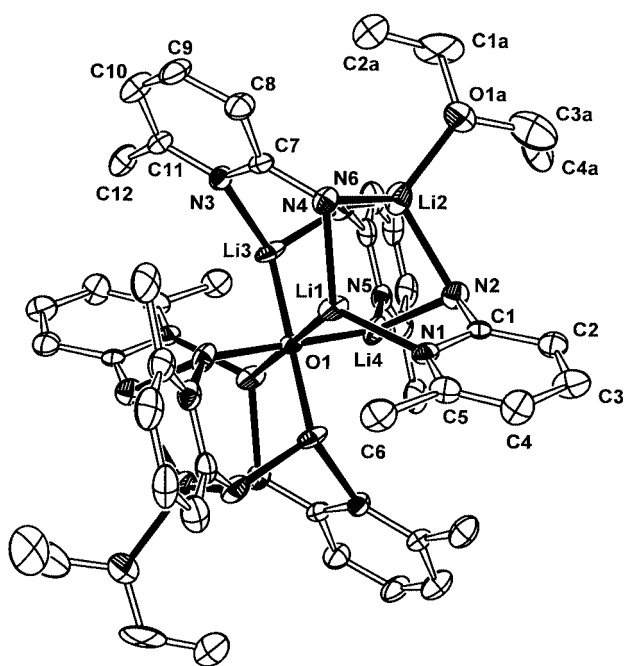
3

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 ^{1}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 v(N–H) stretching frequency is evident in the infrared spectrum at 3677 cm⁻¹. Lithiation of 2-amino-6-methylpyridine with one equivalent of n-BuLi in hexane–tmeda yielded a colourless solution from which colourless [Li(C₅H₃NMeNH)(tmeda)] **2** (Scheme 2) was isolated after removal of the solvent *in vacuo*. For compound **2** the ^{1}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_arom–CH₃ protons respectively, and at δ 2.00 and 1.98 due to the CH₂ and CH₃ protons on the tmeda ligand respectively. The v(N–H) stretch in the infrared was readily identifiable at 3401 cm⁻¹.

While we were unable to obtain crystals of [Li(C₅H₃NMeNH)(Et₂O)ₙ] **1** or [Li(C₅H₃NMeNH)(tmeda)ₙ] **2** it was possible

Table 1 Crystal data and summary of data collection for complexes **3–5**

	3	**4**	**5**
Formula	$C_{44}H_{62}Li_8N_{12}O_3$	$C_{24}H_{37}Li_4N_8O_{0.5}$	$C_{32}H_{52}Li_4N_8O_4Si_4$
Formula weight	862.57	473.38	752.94
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	10.918(1)	11.492(2)	10.766(2)
b/Å	11.4313(8)	13.492(2)	11.486(2)
c/Å	11.709(1)	19.326(3)	18.049(4)
α/°	71.001(8)		93.880(4)
β/°	71.220(9)	103.137(3)	97.690(5)
γ/°	73.495(8)		102.459(4)
V/Å³	1281.7(3)	2917.9(7)	2148.9(8)
Z	1 (dimer)	4	2
μ/mm⁻¹	0.07	0.066	0.12
Reflections collected	4490	13241	9728
Observed reflections	1579	4211 ($R_{int} = 0.0972$)	6152
T/K	296	296	296
R	0.088	0.0549	0.070
R_w	0.074	0.149	0.165

Fig. 1 Molecular structure of the octanuclear centrosymmetric dimer [Li₈(C₅H₃NMeNH)₆(O)(OEt₂)₂], **3**.
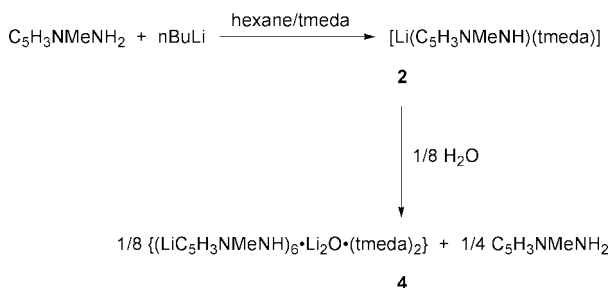
Scheme 2

to grow crystals of some derivatives of compounds **1** and **2** suitable for X-ray diffraction studies. From one reaction in the formation of compound **1**, large colourless crystals were isolated. An X-ray study showed them to be [Li₈(C₅H₃NMeNH)₆(O)(OEt₂)₂], **3**. Compound **3** was deliberately synthesized by treating **1** with water in the correct stoichiometry (Scheme 1). This reaction is as expected, extremely exothermic, requiring cooling in ice to inhibit the possibility of ignition. The ¹H NMR spectrum of **3** is unexceptional but confirms the 3:1 ratio

Table 2 Selected bond distances (Å) and angles (°) for [Li₈(C₅H₃-NMeNH)₆(O)(OEt₂)₂] **3**

|			
Li(1)–O(1)	1.86(1)	Li(3)–O(1)	1.88(1)
Li(1)–N(1)	2.01(1)	Li(3)–N(3)	2.01(1)
Li(1)–N(4)	2.00(1)	Li(3)–N(6)	2.01(2)
Li(2)–N(2)	2.12(1)	Li(4)–O(1)	1.87(1)
Li(2)–N(4)	2.07(1)	Li(4)–N(2)	2.03(2)
Li(2)–N(6)	2.11(1)	Li(4)–N(5)	2.03(1)
Li(2)–O(1a)	1.95(2)	Li(1)–Li(3)	2.58(1)
Li(1)–Li(4)	2.56(2)	Li(3)–Li(4)	2.56(2)
O(1)–Li(1)–N(1)	120.6(6)	O(1)–Li(3)–N(3)	125.4(6)
O(1)–Li(1)–N(4)	116.4(6)	O(1)–Li(3)–N(6)	114.5(6)
N(1)–Li(1)–N(4)	114.5(7)	N(3)–Li(3)–N(6)	109.4(7)
N(2)–Li(2)–N(4)	106.1(7)	O(1)–Li(4)–N(2)	115.3(6)
N(2)–Li(2)–N(6)	103.6(7)	O(1)–Li(4)–N(5)	123.9(6)
N(2)–Li(2)–O(1a)	112.5(7)	N(2)–Li(4)–N(5)	112.2(8)
N(4)–Li(2)–N(6)	107.5(7)	N(4)–Li(2)–O(1a)	117.0(8)
N(6)–Li(2)–O(1a)	109.3(7)	Li(1)–O(1)–Li(1′)	180.0
Li(1)–O(1)–Li(3)	87.4(5)	Li(1)–O(1)–Li(4)	86.9(6)
Li(3)–O(1)–Li(4)	86.3(6)	Li(3)–O(1)–Li(4)	93.7(6)
Li(3)–O(1)–Li(3′)	180.0	Li(4)–O(1)–Li(4′)	180.0

of 2-amino-6-methylpyridine to diethyl ether. Compound **3** crystallises in the triclinic space group $P\bar{1}$ with half a molecule in the asymmetric unit and the central oxygen atom residing on the inversion centre. The overall centrosymmetric structure (Fig. 1, Table 2) comprises an octahedral oxygen atom bound by six lithium atoms (Li(1), Li(3) and Li(4) and their symmetry equivalents). The bidentate ligands do **not** act as chelates to the lithium centres, rather the lithium atoms Li(1) and Li(3) are bridged by N(4), C(7) and N(3), Li(1) by N(1), C(1) and N(2) and Li(3) by N(6), C(13) and N(5) units. Li(2) caps the amido nitrogen atoms N-(2), -(4) and -(6) and is in a tetrahedral environment completed by an O-bound ether molecule. The Li–N (averages are 2.01 Å for the three-co-ordinate Li and 2.10 Å in the four-co-ordinate Li) and Li–O (average of 1.87 Å for the oxide and 1.95 Å for the ether) bonding distances are unexceptional. The Li(1)–N(2), Li(3)–N(4) and Li(4)–N(6) distances are all greater than 2.5 Å and are not considered bonding. Thus, of the four unique lithium centres, three are three-co-ordinate (Li(1), Li(3) and Li(4)) and one is four-co-ordinate (Li(2)). The OLi₆ core structure is similar to several previously reported complexes, *viz.* [Li₂(salen)]₃·Li₂O·2tmeda·H₂O,[10] [Li₁₈(*i*Pr₂(Mes)SiP)₈O],[12] [Li₂₆(Me₂(*i*PrMe₂C)SiAs)₁₂-O],[12] [Li₂(CSiMe₃SO₂Ph)]·Li₂O·10thf,[9] and [Li₁₄{(c-C₅H₉)N-(H)}₁₂(O)] where Li–O–Li angles are close to 90°.[11]

Treatment of [Li(C₅H₃NMeNH)(tmeda)] **2** with a controlled amount of water (Scheme 2) in hexane resulted in a very exothermic reaction from which large colourless crystals of

Table 3 Selected bond distances (Å) and angles (°) for [Li$_8$(C$_5$H$_3$NMeNH)$_6$(O)(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 $-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$.
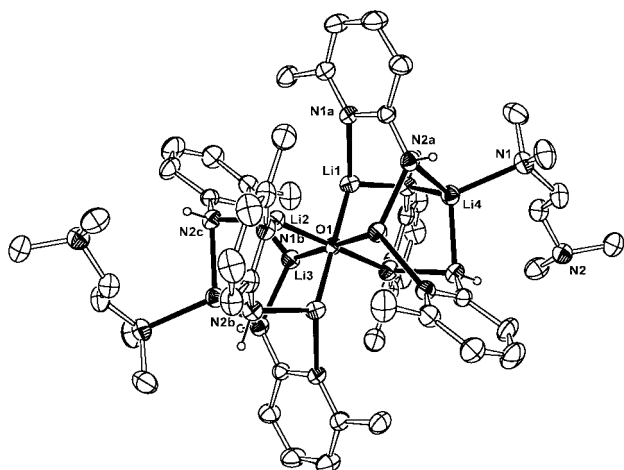
Fig. 2 Molecular structure of [Li$_8$(C$_5$H$_3$NMeNH)$_6$(O)(tmeda)$_2$] **4**, with an octahedral central oxygen and a "dangling" tmeda ligand.
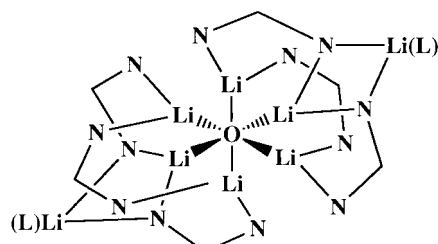
3 L = Et$_2$O
4 L = η^1-tmcda

[Li$_8$(C$_5$H$_3$NMeNH)$_6$(O)(tmeda)$_2$] **4** were isolated (Fig. 2, Table 3). The overall structure of compound **4** is similar to that of **3** where a central OLi$_6$ fragment is observed. In place of the co-ordinated Et$_2$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 OLi$_6$ core as a feature in its structural motif, *viz.* [Li$_2$(salen)]$_3$·Li$_2$O·2tmeda·H$_2$O.[10] 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 [Li$_4$(C$_5$H$_3$-NMeNHSiMe$_2$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[6a] 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.[5] 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 [Li$_4$(C$_5$H$_3$NMeNH-SiMe$_2$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-

$$[\text{LiC}_5\text{H}_3\text{NMeNH}] + (\text{SiMe}_2\text{O})_n \xrightarrow{\text{Et}_2\text{O}} \{[(\text{C}_5\text{H}_3\text{NMeNHSiMe}_2\text{O})_4]\text{Li}_4\}$$

5
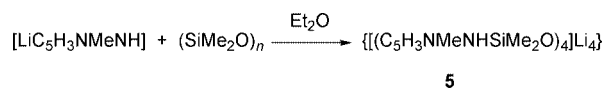
Scheme 3

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
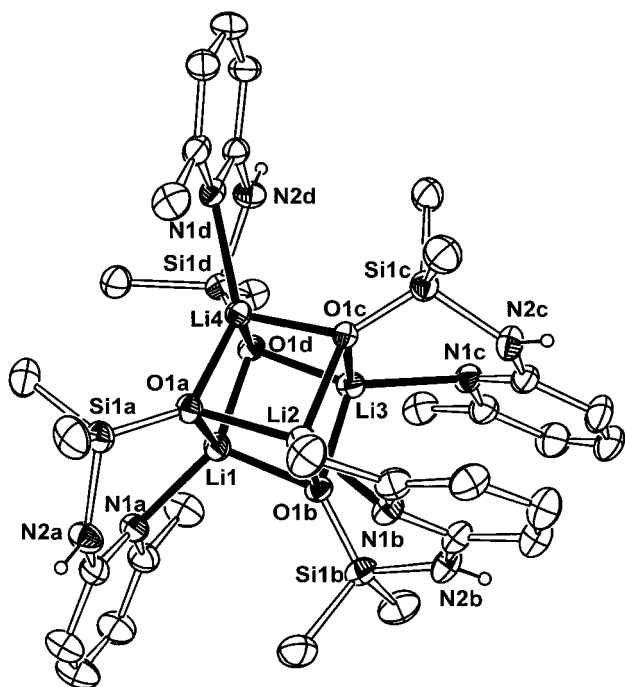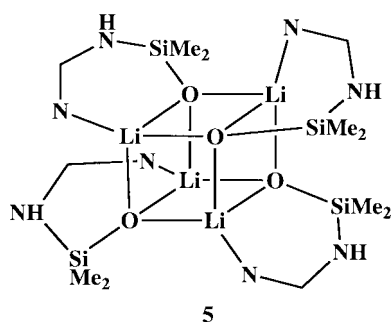
Fig. 3 Molecular structure of tetranuclear [Li$_4$(C$_5$H$_3$NMeNHSi-Me$_2$O)$_4$] **5**.

5

asymmetric unit consists of a tetranuclear aggregate comprised of four C$_5$H$_3$NMeNHSiMe$_2$O$^-$ ligands and four lithium atoms with an Li$_4$O$_4$ pseudo-cubane core as the main structural feature. In contrast to the chemistry we observed for the quinoline chemistry,[5] where insertion of SiMe$_2$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),[5] although there have been reports of similar SiMe$_2$O insertions into Ln–N bonds (Ln = Ho, Dy or Yb).[14,15] 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.[14,15] A related complex with an Li$_4$O$_4$ cubane core has been observed from the treatment of tBu$_2$Si(NH$_2$)OH with butyllithium yielding [tBu$_2$Si(NH$_2$)OLi]$_4$.[21] In the present Li$_4$O$_4$ core the bond lengths and angles are very similar to those in [tBu$_2$Si(NH$_2$)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 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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