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Synthesis and structural studies of an (8-quinolyl)amido-lithium complex and its reaction with dimethylsilicone

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Dedicated to Professor Martin Bennett for his fine contributions to organometallic chemistry throughout his outstanding career.

Abstract

Treatment of 8-aminoquinoline (AQH$_2$) with ^{n}BuLi in diethyl ether affords {[(AQH)$_2$]Li$_2$(OEt$_2$)}$_2$ (**1**). Compound **1** reacts with dimethylsilicone to yield the lithiated SiMe$_2$-bridged complex, {[(AQ)$_2$SiMe$_2$]Li$_2$(OEt$_2$)}$_2$ (**2**). Compound **2** has also been synthesised by treating **1** with dichlorodimethylsilane affording {[(AQH)$_2$SiMe$_2$] (**3**), followed by dilithiation. All complexes were characterised by spectroscopic and X-ray crystallographic methods. The X-ray structure of **1** reveals a tetranuclear centrosymmetric dimeric structure with a Li$_4$N$_4$ step-ladder arrangement. Compound **2** is tetranuclear with an eight-membered Li$_4$N$_4$ ring with ligands straddling Li atoms at opposing corners of the ring. Compound **3** has a SiMe$_2$ group bridging two 8-amidoquinoline functionalities. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium; 8-Aminoquinoline; Dimethylsilicone

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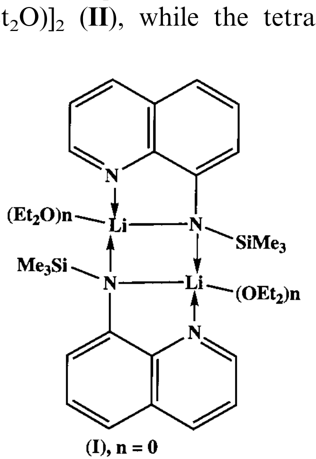
1. Introduction

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 Brønsted bases or nucleophiles in organic synthesis [2]. The structural elucidation 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. The high polarity of Li–N bonds causes compounds to associate [3], unless prevented by bulky substituents and this degree of aggregation has been intensely studied recently [4].

In this paper we report the synthesis and structural studies of an N-functionalised amido-lithium compound based on 8-aminoquinoline (AQH$_2$) and its reactivity with dimethylsilicone. This work is related to work we have previously published in the substantially more sterically hindered 8-(trimethylsilyl)aminoquinoline (TMSAQH) system where a number of organoamide complexes have been synthesised [5–7]. 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 (TMSAQ$^-$), centrosymmetric dimers dominate, for example in the unsolvated [(TMSAQ)Li]$_2$ (**I**), and the etherate [(TMSAQ)Li(Et$_2$O)]$_2$ (**II**), while the tetramethylethye-



(I), n = 0
(II), n = 1

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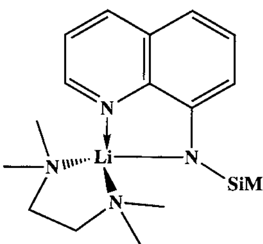
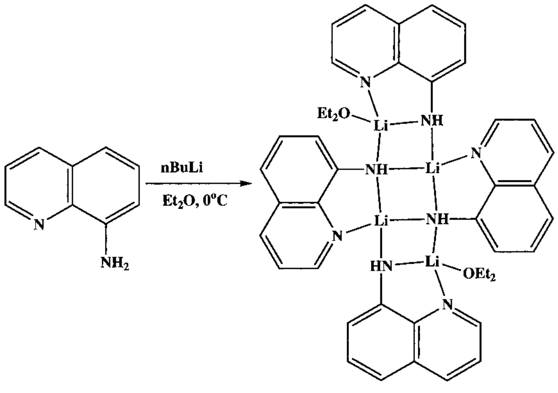
lenediamine adduct is monomeric, [(TMSAQ)-Li(tmeda)] (**III**) [5]. In the absence of TMS groups higher aggregates can be expected.



(**III**)

Of additional interest in organoamide chemistry is the reactivity of M–N bonds. Recently, there has been interest in the reaction of organometallic and organoamide complexes with dimethylsilicone. The general reaction involves the insertion of Me_2SiO into the Ln–N bond, e.g. $[(CpMe)Yb(pzMe_2)(OSiMe_2pzMe_2)]_2$ [8] and $[CpHo(pzMe_2)(OSiMe_2pzMe_2)]_2$ [9]. Furthermore, TlOEt is known to react with dimethylsilicone polymer, generating $[\{Tl_2(OSiMe_2)_2O\}]_n$ [10].

Herein, we report the synthesis of lithiated 8-aminoquinoline, and its serendipitous reaction with dimethylsilicone. A deliberate synthesis of the latter complex is also reported.



Scheme 1.

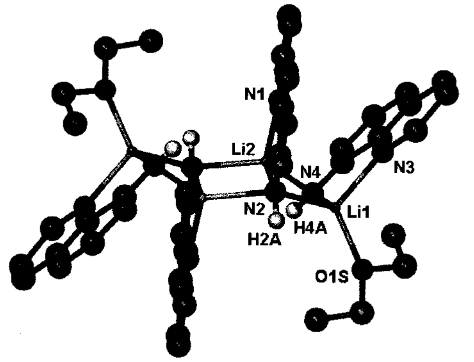


Fig. 1. Molecular structure of the centrosymmetric dimer $\{[(AQH)_2]Li_2(OEt_2)\}_2$ (**1**).

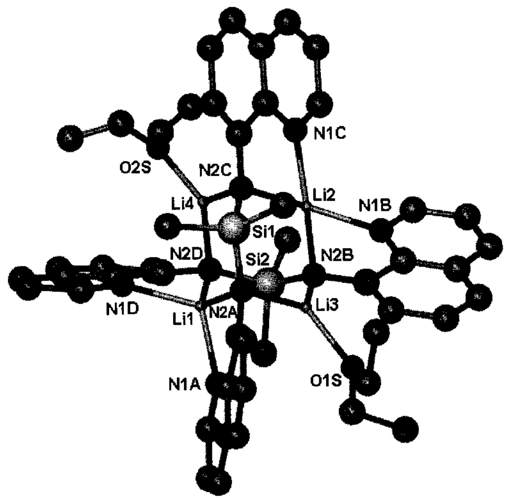


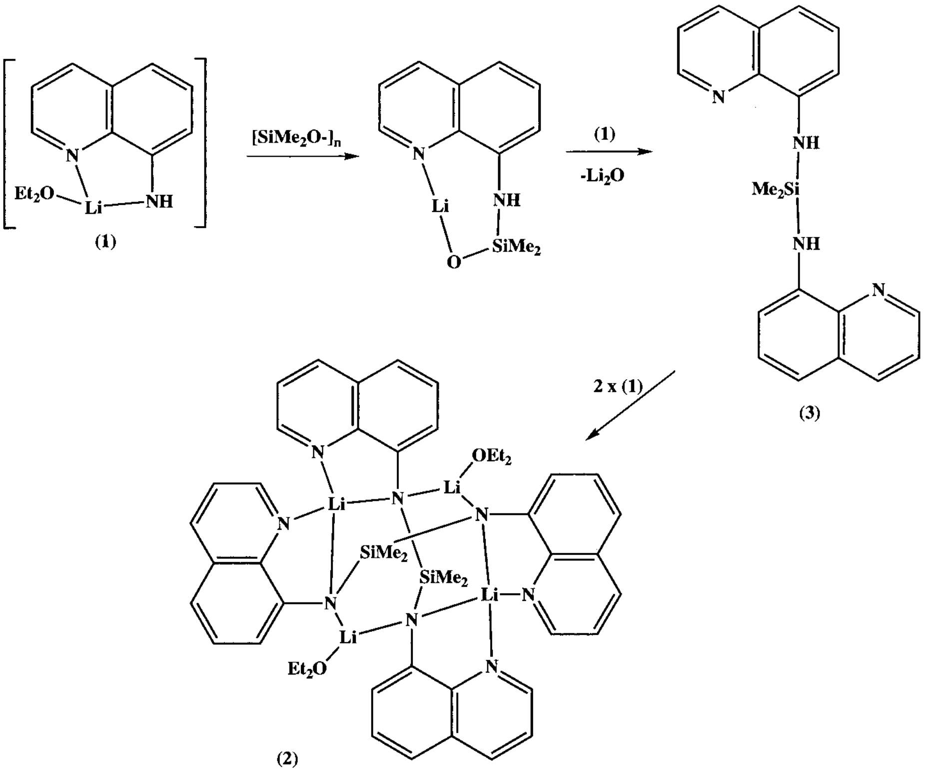
Fig. 2. Molecular structure of tetranuclear $\{[(AQ)_2SiMe_2]Li_2(OEt_2)\}_2$ (**2**).

2. Experimental

8-Aminoquinoline, dichlorodimethylsilane and ^nBuLi (1.8 or 2.5 M solutions in hexane) were purchased from Aldrich and used as received. Diethyl ether was dried over CaH_2 then freshly distilled from sodium/benzophenone and all manipulations were performed using conventional Schlenk or glovebox 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. ^1H-NMR spectra were recorded at 300.13 MHz and ^{13}C-NMR spectra were recorded at 75.46 MHz using a Bruker BZH 300/52 spectrometer with a Varian console and chemical shifts were referenced against solvent. Mass spectra were recorded on a VG platform II mass spectrometer using atmospheric pressure chemical ionisation conditions and a CH_2Cl_2 matrix. Melting points were determined in sealed glass capillaries under argon.

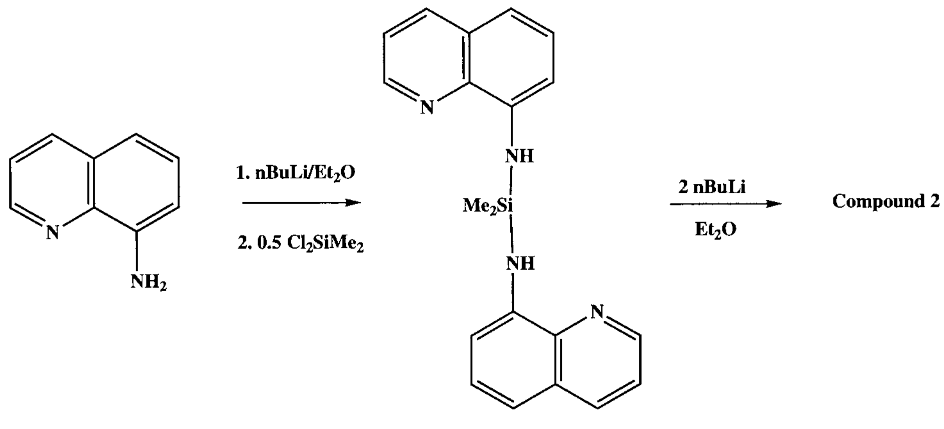
2.1. Preparation of $\{[(AQH)_2]Li_2(OEt_2)\}_2$ (1)

^nBuLi (1.4 ml, 2.5 M, 3.5 mmol) was added in a dropwise fashion to a solution of 8-aminoquinoline (0.5 g, 3.5 mmol) in diethyl ether (30 cm^3) at 0°C, forming an intense red solution. The solution was reduced in volume in vacuo to the point of crystallisation, and placed at −35°C overnight, yielding orange crystals. Yield, 0.35 g, 47%; m.p. 285–287°C. ^1H-NMR (300 MHz, C_6D_6, 298 K): δ 1.11 (t, 12H, CCH_3), 3.23 (q, 8H, CH_2), 4.62 (s, 4H, NH), 6.4–8.4 (m, 24H, aromatics). ^{13}C-NMR (75.46 MHz, C_6D_6, 298 K): δ 16.58 (CH_3), 66.31 (CH_2), 109.28, 109.88, 115.66, 121.63, 129.57, 136.00, 139.25, 144.11, 147.44 (aromatics). APCI mass spectrum (m/z): 145 [AQ^+] (10%). IR



(2)

Scheme 2.



(3)

Scheme 3.

(Nujol, ν): 3490, 1614, 1592, 1565, 1504, 1321, 1248, 1094, 974, 918, 818, 789, 738, 645 cm^{-1}.

2.2. Preparation of $\{[(AQ)_2SiMe_2]Li_2(OEt_2)\}_2$ (2)

In one reaction of forming compound **1**, several bright red crystals were observed. These were hand-picked from the mixture and an X-ray crystal structure was performed on these crystals. Compound **2** was deliberately synthesised as follows: ^{n}BuLi (1.4 ml, 2.5 M, 3.5 mmol) was added to a diethyl ether (30 cm^3) solution of compound **3** (0.6 g, 1.75 mmol) at 0°C, resulting in the formation of a deep red precipitate in a deep red solution. M.p. 70°C (dec.). ^{1}H-NMR (300

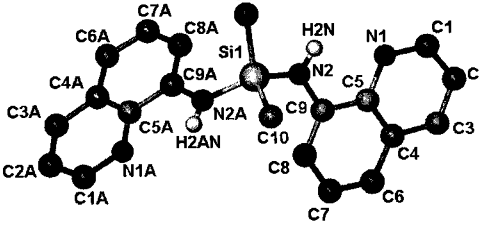


Fig. 3. Molecular structure of $[(AQH)_2SiMe_2]$ (**3**).

Table 1
Crystal data and summary of data collection for complexes **1**–**3** [a]

Compound	$\{[(AQH)_2]Li_2(OEt_2)\}_2$ (**1**)	$\{[(AQ)_2SiMe_2]Li_2(OEt_2)\}_2$ (**2**)	$[(AQH)_2SiMe_2]$ (**3**)
Molecular formula	$C_{48}H_{58}N_8O_3Li_4$	$C_{48}H_{56}N_8O_2Si_2Li_4$	$C_{20}H_{20}N_4Si$
Formula weight	822.81	860.96	344.49
$F(000)$	438.0	1824.0	728.0
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	11.174(2)	13.149(2)	10.996(1)
b (Å)	11.336(1)	20.617(2)	11.370(1)
c (Å)	11.620(2)	18.821(3)	14.977(2)
α (°)	90.19(1)	90	90
β (°)	109.79(2)	105.33(1)	101.841(9)
γ (°)	118.18(2)	90	90
V (Å^3)	1196.8(5)	4921(1)	1832.6(4)
Z	1 (dimer)	4	4
D_{calc} (g cm^{-3})	1.141	1.162	1.248
μ (mm^{-1})	0.07	0.12	0.14
Absorbance (min., max.)	1.033, 1.055	1.042, 1.058	1.050, 1.060
Crystal size (mm)	0.80 × 0.38 × 0.68	0.48 × 0.46 × 0.40	0.58 × 0.32 × 0.20
Colour	Orange	Red	Colourless
Reflections collected	4442	9341	3589
Reflections Observed	1629	2808	1928
Parameters	276	578	227
R	0.082	0.084	0.053
R_w	0.085	0.074	0.061

[a] Data common to all compounds: Enraf–Nonius CAD4 diffractometer, Mo–K$_\alpha$ radiation, 2–50° 2θ range, 3σ cut-off, data collected at 296 K.

MHz, C_6D_6, 298 K): δ 0.02 (s, 6H, Si(CH_3)$_2$), 1.15 (t, 12H, CCH_3), 3.29 (q, 8H, CH_2), 6.4–8.4 (m, 24H, aromatics). APCI mass spectrum (m/z): 204 [HAQSiMe$_2^+$], 189 [HAQSiMe$^+$], 146 [HAQ$^+$].

2.3. Preparation of {[(AQH)$_2$SiMe$_2$] (**3**)

^{n}BuLi (3.86 ml, 1.8 M, 6.94 mmol) was added in a dropwise fashion to a solution of 8-aminoquinoline (1.0 g, 6.94 mmol) in diethyl ether (30 cm^3) at 0°C, forming a deep red solution. To the solution was added Me_2SiCl_2 (1.41 ml, 3.47 mmol), forming a yellow solution and a white precipitate. Filtration afforded a yellow solution that was reduced in volume in vacuo to the point of crystallisation and placed at −35°C overnight, yielding colourless crystals. Yield 1.01 g, 80%; m.p. 133–4°C. ^{1}H-NMR (300 MHz, C_6D_6, 298 K): δ 0.41 (s, 6H, Si(CH_3)$_2$), 4.66 (s, 2H, NH), 6.70–8.59 (m, 12H, aromatics). ^{13}C-NMR (75.46 MHz, C_6D_6, 298 K): δ −1.17 (Si(CH$_3$)$_2$), 109.55, 110.95, 115.98, 121.33, 129.23, 136.00, 139.98, 144.80, 146.94 (aromatics). APCI mass spectrum (m/z): 145 [AQ$^+$] (100%), 188 [AQSiMe$^+$] (100%), 203 [AQSiMe$_2^+$] (25%), 327 [(AQ)$_2$SiMeH$^+$]. IR (Nujol, ν): 3325, 1610, 1590, 1571, 1505, 1412, 1317, 1254, 1091, 1059, 919, 793, 657, 583 cm^{-1}.

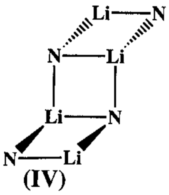
2.4. Collection of X-ray diffraction data, and solution and refinement of the structures

For compounds **1**–**3** the room temperature data sets were acquired on an Enraf–Nonius CAD4 diffractometer on capillary mounted specimens (2θ max. = 50°, scan mode = $2\theta/\theta$; monochomatic Mo–K$_\alpha$ radiation, $\lambda = 0.7107_3$ Å; $T \sim 295$ K) yielding N independent reflections, N_o with $I > 3\theta(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$, R, R_w (statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ are quoted. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system implemented by Hall [11]. In compound **1**, a molecule of diethyl ether was located in the lattice which was disordered, but was successfully refined. The crystal decomposed slightly during data collection (approx. 10%). Compound **2** decomposed significantly (approx. 30%) during data collection leading to a structure of low precision, but the connectivity is unquestionable in this complex.

3. Discussion

Lithiation of 8-aminoquinoline (AQH$_2$) with one equivalent of ^{n}BuLi in diethyl ether at 0°C rapidly formed an orange–red solution (Scheme 1). Crystallisation of the product afforded large orange crystals of $\{[(AQH)_2]Li_2(OEt_2)\}_2$ (**1**) in moderate yield. Compound **1** is thermally robust with a melting point of 285°C. The ^{1}H-NMR spectrum displays a resonance for the N–H protons at 4.65 ppm, which is upfield of the free ligand (5.15 ppm). Resonances occur between 6.5 and 8.7 ppm for the aromatic protons. The resonances for the coordinated diethyl ether protons occur at 1.11 and 3.23 ppm, which are slightly shifted from those for free diethyl ether (1.1 and 3.5 ppm). The ^{13}C-NMR spectrum is unexceptional with aromatic resonances between 109.8 and 147.4 ppm and the diethyl ether resonances at 16.08 and 66.31 ppm. The only identifiable peak in the APCI mass spectrum corresponds to the protonated ligand at a mass/charge ratio of 145 Da.

Compound **1** crystallises in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. A disordered diethyl ether molecule resides in the lattice. The tetranuclear dimeric molecule resides on a crystallographic inversion centre with a $Li_4(AQH)_4$ core which is solvated by two diethyl ether molecules (Fig. 1). The Li_4N_4 unit exists as a step-ladder arrangement, **(IV)** which is rather common in lithium amide chemistry [12]. The existence of a tetranuclear complex rather than a dinuclear arrangement in the trimethylsilyl analogue, $[8\text{–}SiMe_3AQLi(Et_2O)]_2$ is a consequence of the lower steric hindrance afforded by the ligand at the amido nitrogen centre. The amidoquinoline group acts as a bidentate ligand to all lithium centres and each amido group also bridges to another lithium atom, with the terminating lithiums being solvated by a diethyl ether molecule, thus each lithium centre is four-coordinate. The Li–N bond distances in **1** ($\text{Li–N}_{(amido)}$, range 1.982(9)–2.11(1) Å and $\text{Li–N}_{(aromatic)}$, range 2.03(2)–2.06(1) Å) are similar to its silylated analogue $[8\text{-}SiMe_3AQLi(Et_2O)]_2$, ($\text{Li–N}_{(amido)}$ 2.07(2) Å and $\text{Li–N}_{(aromatic)}$, 2.03(2) Å) [5], but in the latter, the bridging Li–N distance is much longer (Li(N), 2.21(2)) [5]. The Li–O distance 2.01(1) Å in compound **1** is slightly longer than in its silylated analogue (1.94(3) Å) and for example in $[\{Li(OEt_2)[\mu\text{-}N(SiMe_3)_2]\}_2]$ (1.943(6) Å) [13,14].



(IV)

Table 2
Selected bond lengths (Å) and angles (°) for $\{[(AQH)_2]Li_2(OEt_2)\}_2$ (**1**)

Bond lengths			
Li(1)–O(1s)	2.01(1)	Li(2)–N(1)	2.03(2)
Li(1)–N(2)	2.11(1)	Li(2)–N(2)	2.050(9)
Li(1)–N(3)	2.06(1)	Li(2)–N(4)	2.03(1)
Li(1)–N(4)	1.982(9)	Li(2)–N(2′)	2.11(1)
Li(1)–Li(2)	2.39(1)	Li(2)–Li(2)	2.45(2)
N(2)–H(2a)	1.014(5)	N(4)–H(4a)	1.035(5)
Bond angles			
N(2)–Li(1)–N(3)	117.3(7)	N(1)–Li(2)–N(2)	84.0(5)
N(2)–Li(1)–N(4)	105.6(5)	N(1)–Li(2)–N(4)	123.4(6)
N(2)–Li(1)–O(1s)	106.5(5)	N(1)–Li(2)–N(2′)	111.7(6)
N(3)–Li(1)–N(4)	84.6(4)	N(2)–Li(2)–N(4)	106.0(5)
N(3)–Li(1)–O(1s)	117.3(5)	N(2)–Li(2)–N(2′)	107.9(5)
N(4)–Li(1)–O(1s)	124.6(8)	N(4)–Li(2)–N(2′)	117.0(6)
Li(1)–N(2)–Li(2)	70.1(4)	Li(2)–N(2)–Li(2′)	72.1(4)
Li(1)–N(2)–Li(2′)	127.8(5)	Li(2)–N(1)–C(1)	131.2(6)
Li(1)–N(4)–Li(2)	73.0(5)	Li(2)–N(1)–C(5)	109.9(5)
Li(1)–N(2)–C(9)	118.9(5)	Li(2)–N(2)–C(9)	109.1(5)
Li(1)–N(2)–H(2a)	90.9(5)	Li(2)–N(2)–H(2a)	133.8(6)
Li(1)–N(3)–C(10)	133.6(4)	Li(2)–N(2)–C(9)	106.7(5)
Li(1)–N(3)–C(14)	108.2(5)	Li(2)H(2a)–N(2)–H(2a)	90.2(4)
Li(1)–N(4)–C(18)	110.4(5)	Li(2)–N(4)–C(18)	112.6(6)
Li(1)–N(4)–H(4a)	132.4(5)	Li(2)–N(4)–H(4a)	105.8(5)
Li(1)–O(1s)–C(1s)	115.0(6)		
Li(1)–O(1s)–C(3s)	124.2(5)		

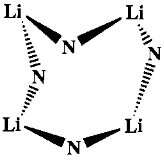
Table 3
Selected bond lengths (Å) and angles (°) for $\{[(AQ)_2SiMe_2]\text{-}Li_2(OEt_2)\}_2$ (**2**)

Bond lengths			
Li(1)–N(1a)	2.1(1)	Li(2)–N(1b)	2.1(1)
Li(1)–N(2a)	2.1(1)	Li(2)–N(2b)	2.0(1)
Li(1)–N(1d)	2.0(1)	Li(2)–N(1c)	2.1(1)
Li(1)–N(2d)	1.9(1)	Li(2)–N(2c)	2.1(1)
Li(3)–N(2c)	2.05(9)	Li(4)–N(2a)	1.9(1)
Li(3)–N(2d)	2.05(9)	Li(4)–N(2b)	2.0(1)
Li(3)–O(1s)	1.9(1)	Li(4)–O(2s)	2.0(1)
Li(1)–Li(2)	3.7(1)	Li(2)–Li(3)	2.7(1)
Li(1)–Li(3)	2.7(1)	Li(2)–Li(4)	2.7(1)
Li(1)–Li(4)	2.8(1)	Li(3)–Li(4)	4.0(1)
Bond angles			
N(1a)–Li(1)–N(1d)	119(5)	N(1b)–Li(2)–N(1c)	123(5)
N(1a)–Li(1)–N(2d)	128(5)	N(1b)–Li(2)–N(2c)	129(5)
N(2a)–Li(1)–N(1d)	125(6)	N(2b)–Li(2)–N(1c)	137(6)
N(2a)–Li(1)–N(2d)	131(5)	N(2b)–Li(2)–N(2c)	124(5)
N(1d)–Li(1)–N(2d)	87(5)	N(1c)–Li(2)–N(2c)	81(5)
N(2c)–Li(3)–N(2d)	123(6)	N(2a)–Li(4)–N(2b)	124(5)
N(2c)–Li(3)–O(1s)	135(5)	N(2a)–Li(4)–O(2s)	126(5)
N(2d)–Li(3)–O(1s)	116(5)	N(2b)–Li(4)–O(2s)	114(5)
Li(1)–N(2d)–Li(3)	84(5)	Li(2)–N(2c)–Li(3)	82(5)
Li(1)–N(2a)–Li(4)	89(5)	Li(2)–N(2b)–Li(4)	80(5)

Table 4
Selected bond lengths (Å) and angles (°) for $[(AQH)_2SiMe_2]$ (**3**)

Bond lengths			
N(2)–Si(1)	1.732(3)	N(2a)–Si(1)	1.720(3)
N(2)–H(2n)	1.015(3)	N(2a)–H(2an)	1.036(3)
Si(1)–C(10)	1.842(5)	Si(1)–C(11)	1.843(4)
Bond angles			
C(9)–N(2)–Si(1)	129.8(3)	C(9a)–N(2a)–Si(1)	131.3(3)
C(9)–N(2)–H(2n)	118.9(3)	C(9a)–N(2a)–H(2an)	114.6(3)
Si(1)–N(2)–H(2n)	111.1(2)	Si(1)–N(2a)–H(2an)	114.1(2)
N(2)–Si(1)–N(2a)	111.9(1)	C(10)–Si(1)–C(11)	112.4(2)
N(2)–Si(1)–C(10)	112.0(2)	N(2a)–Si(1)–C(10)	104.7(2)
N(2)–Si(1)–C(11)	104.1(2)	N(2a)–Si(1)–C(11)	112.0(2)

During the synthesis of compound **1**, a second crystal morphology and colour was observed. These crystals were isolated by hand-picking and were examined by X-ray diffraction. Compound **2** crystallises in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The asymmetric unit consists of a dinuclear aggregate comprised of two $[(AQ)_2SiMe_2)]^{2-}$ ligands, four lithium atoms and two diethyl ether molecules of solvation (Fig. 2). As found in compound **1**, the central unit consists of a Li_4N_4 core, but in contrast with **1**, the core exists as a Li_4N_4 eight-membered ring (**V**), rather than the step-ladder structure found in **1**. This type of arrangement is rather rare in lithium amido chemistry, but examples can be found in the literature, viz. $[Li(pip)]_4$, (pip = 2,2,6,6-tetramethylpiperidinato) [14] and $[Cy_2NLi]_4$, (Cy = cyclohexyl) [15]. In the former, the Li_4N_4 ring is essentially planar, while in the latter, it is slightly skewed in a butterfly configuration. Compound **2** has a much more distorted conformation, and this is probably due to the straddling effect of opposite 'corners' of the eight-membered ring by the $SiMe_2$ groups which strap the aminoquinoline ligands together. All four lithium centres are coplanar (within estimated S.D.) and alternate nitrogen centres are above and below this plane (**V**). All $N_{(amido)}$ centres in **2** are bridging and there are two four-coordinate Li atoms (bound to two aromatic N and two bridging amido N) and two three-coordinate Li atoms (bound to two bridging amido N and one ether O atom). The $Li–N_{(amido)}$ distances average 2.0 Å which is in accordance with established Li–N(bridging) distances in $[Li(pip)]_4$, (2.00(2) Å) [14] and $[Cy_2NLi]_4$, (1.96 Å) [15]. The Li–N(aromatic) distances (av. 2.1(1) Å) are similar to compound **1** above (range 2.03(2)–2.06(1) Å). The Li–O distances (1.9(1) and 2.0(1) Å are similar (2.01(1) Å) to that in compound **1**. The N–Li–N angles in compound **2** range from 81 to 137° whereas in the planar eight-membered ring of $[Li(pip)]_4$ they average 168.5° [14] and in $[Cy_2NLi]_4$, the angles are rather constant with a similar average of 168.3° [15]. The Li–N–Li angles in compound **2** range from 80 to 89°.



(V)

The formation of **2** is rather intriguing but has been attributed to compound **1** coming into contact with adventitious dimethylsilicone grease ($[SiMe_2O]_n$) which was being used as a lubricant in ground glass stopcocks. This polymer has good solubility in organic solvents and it is evident that small amounts can easily migrate into the reaction mixture. The reaction of organometallic species with dimethylsilicone grease is not without precedent, and some unusual results have been obtained [8–10]. The postulated mechanism in the formation of compound **2** is outlined in Scheme 2. Lithiated 8-aminoquinoline initially reacts with the polymer and insertion of dimethylsilicone into the Li–N bond occurs. This insertion complex reacts further with excess compound **1** in solution to eliminate Li_2O with subsequent formation of the $SiMe_2$ bridged aminoquinoline $[(AQH)_2SiMe_2]$. Introduction of the $SiMe_2$ group to the amino nitrogen centres increases the thermodynamic acidity of the proton on the amine, and excess compound **1** acts as a lithiating reagent to dilithiate $[(AQH)_2SiMe_2]$.

An intentional synthesis of compound **2** was subsequently achieved in a separate experiment (Scheme 3). Thus, half an equivalent of dimethyldichlorosilane was added to a diethyl ether solution of **1**. The deep orange solution immediately turned yellow with concurrent formation of a white precipitate. Isolation of the reaction mixture by filtration and crystallisation afforded colourless crystals of $[(AQH)_2SiMe_2]$, (**3**) (Fig. 3). Dilithiation of **3** was achieved by addition of two equivalents of ^{n}BuLi in diethyl ether at 0°C, yielding a deep red solution. The ^{1}H-NMR spectrum supported the formation of **2** with a single resonance at 0.02 ppm, resonances at 1.15 and 3.29 ppm due to diethyl ether and aromatic resonances at 6.4–8.4 ppm. There was no resonance due to N–H evident in the infrared spectrum. The complex has low moisture and thermal stability, resulting in rapid decomposition upon exposure to air and above 70°C. The only identifiable peaks in the APCI mass spectrum were for $[(AQH)SiMe_2^+]$, $[(AQH)SiMe^+]$ and $[AQH^+]$.

Compound **3** is remarkably (given the ease of hydrolysis of silylated amines) stable to decomposition with no signs of decomposition over several days exposure to the atmosphere. The ^{1}H-NMR spectrum show has a singlet at 0.41 ppm due to the protons on the $SiMe_2$ group (dimethylsilicone grease has a single resonance at 0.29 ppm), a broad singlet at 4.7 ppm for the N–H proton and aromatic resonances from 6.70 to 8.59 ppm. The ^{13}C-NMR spectrum is unexceptional with a sharp characteristic peak at -1.77 ppm due to the carbons on the $SiMe_2$ group. The infrared spectrum shows an absorbance at 3325 cm^{-1} attributable to ν(N–H). No molecular ion of complex **3** was observed in the APCI mass spectrum, although peaks corresponding to $[(AQH)SiMe_2^+]$, $[(AQH)SiMe^+]$ and (AQH^+) were identifiable.

Single crystals of compound **3** (Fig. 3) were grown from diethyl ether and crystallise in the monoclinic space group $P2_1/n$ with one whole molecule comprising the asymmetric unit and four molecules in the unit cell. The Si atom is close to tetrahedral with Si–N distances of 1.720(5) and 1.732(6) Å and Si–C distances of 1.842(5) and 1.843(4) Å. The angle between the planes defined by each of the aromatic rings is 78.5(3)°.

4. Conclusions

We have established some interesting structural chemistry and reactivity of nitrogen-functionalised lithium amides. Lowering the steric bulk (by exclusion of the trimethylsilyl groups) of the bidentate 8-aminoquinoline increases the aggregation of the lithium amide from a dimeric species to a tetranuclear complex with a Li_4N_4 step-ladder arrangement. The lithium amide reacts with dimethylsilicone polymer to produce a novel $SiMe_2$ bridged aminoquinoline ligand. Lithiation of this ligand affords another tetranuclear lithium amide with a Li_4N_4 eight-membered ring system.

5. Supplementary material

Crystal data and a summary of data collection appear in Table 1 and pertinent results are shown in Tables 2–4 and the Figures; Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 140993 for compound **1**, CCDC 140994 for compound **2** and CCDC 140995 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloid Amides, Ellis Horwood, Chichester, UK, 1980.

[2] (a) M. Majewski, D.M. Gleave, J. Organomet. Chem. 470 (1994) 1 and references therein. (b) B.J. Wakefield, Organolithium Methods, Academic Press, New York, 1988. (c) A.M. Sapsa, P.v.R. Schleyer (Eds.), Lithium Chemistry: A Theoretical and Experimental Overview, Wiley-Interscience, New York, 1995. (d) M. Gray, M. Tinkl, V. Snieckus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, second ed., vol. 11, Pergamon, Oxford, 1995, p. 1 (Chapter. 1). (e) C.H. Heathcock, in: E. Buncel, T. Durst (Eds.), Comprensive Carbanion Chemistry, vol. B, Elsevier, New York, 1980 (Chapter 4).

[3] W.N. Setzer, P.v.R. Schleyer, Adv. Organomet. Chem. 24 (1985) 353.

[4] (a) K. Gregory, P.v.R. Schleyer, R. Snaith, Adv. Inorg. Chem. 37 (1991) 47. (b) R.E. Mulvey, Chem. Soc. Rev. 20 (1991) 176. (c) D.S. Wright, M.A. Beswick, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, second ed., vol. 1, Pergamon, Oxford, 1995, p. 1 (Chapter 1). (d) D. Seebach, Angew. Chem. Int. Ed. Engl. 27 (1988) 1624. (e) D.R. Armstrong, D. Barr, W. Clegg, R.E. Mulvey, D. Reed, R. Snaith, K. Wade, J. Chem. Soc. Chem. Commun. (1986) 869. (f) T. Fjeldberg, P.B. Hitchcock, M.F. Lappert, A.J. Thorne, J. Chem. Soc. Chem. Commun. (1984) 822.

[5] L.M. Engelhardt, G.E. Jacobsen, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1988) 1011.

[6] L.M. Engelhardt, G.E. Jacobsen, P.C. Junk, C.L. Raston, A.H. White, J. Chem. Soc. Chem. Commun. (1990) 89.

[7] L.M. Engelhardt, P.C. Junk, W.C. Patalinghug, R.E. Sue, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc. Chem. Commun. (1991) 930.

[8] X.G. Zhou, H.Z. Ma, X.Y. Huang, X.Z. You, J. Chem. Soc. Chem. Commun. (1995) 2483.

[9] X.G. Zhou, Z.E. Huang, R.F. Cai, L.B. Zhang, L.X. Zhang, Organometallics 18 (1999) 4128.

[10] S. Harvey, M.F. Lappert, C.L. Raston, B.W. Skelton, G. Srivastava, A.H. White, J. Chem. Soc. Chem. Commun. (1988) 1216.

[11] S.R. Hall, G.S.D. King, J.M. Stewart, (Eds.), XTAL 3.4 Users Manual, University of Western Australia, Lamb, Perth, Australia.

[12] (a) G. Boche, I. Langlotz, M. Marsch, K. Harms, N.E.S. Nudelman, Angew. Chem. Int. Ed. Engl. 31 (1992) 1205. (b) M.G. Gardiner, C.L. Raston, Inorg. Chem. 35 (1996) 4047. (c) B.L. Lucht, D.B. Collum, J. Am. Chem. Soc. 118 (1996) 3529. (d) R.E. Hem. Soc. Rev. 27 (1998) 339. (e) G.R. Kowach, C.J. Warren, R.C. Haushalter, F.J. DiSalvo, Inorg. Chem. 37 (1998) 156.

[13] L.M. Engelhardt, A.S. May, C.L. Raston, A.H. White, J. Chem. Soc. Dalton Trans. (1983) 1671.

[14] M.F. Lappert, M.J. Slade, A. Singh, J.L. Atwood, R.D. Rogers, R. Shakir, J. Am. Chem. Soc. 105 (1983) 302.

[15] J. Jubb, P. Berno, S. Hao, S. Gambarotta, Inorg. Chem. 34 (1995) 3563.