

May C. Copsey,<sup>a</sup> Maravanji S. Balakrishna<sup>b</sup> and Tristram Chivers<sup>a\*</sup><sup>a</sup>Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada T2N 1N4, and <sup>b</sup>Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India

Correspondence e-mail: chivers@ucalgary.ca

## Key indicators

Single-crystal X-ray study  
 $T = 173\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
Disorder in main residue  
 $R$  factor = 0.058  
 $wR$  factor = 0.148  
Data-to-parameter ratio = 15.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## A lithium complex of a bis(amido)bis(imido)-silicate dianion

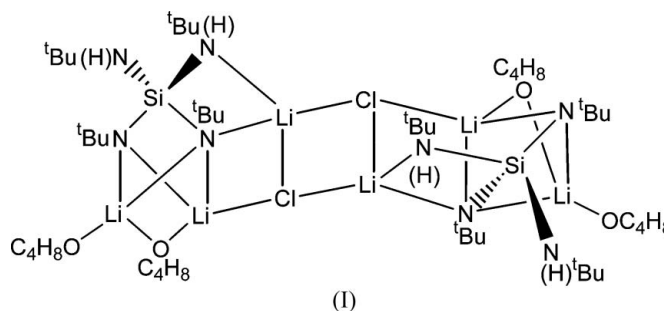
The title compound, bis[ $\mu_3$ -bis(*tert*-butylamido)bis(*tert*-butylimido)silyl]di- $\mu_3$ -chloro-tetrahydrofuranhexalithium(I),  $[\text{Li}_6(\text{C}_{16}\text{H}_{38}\text{N}_4\text{Si})_2\text{Cl}_2(\text{C}_4\text{H}_8\text{O})_4]$ , crystallizes as a dimer of two contact ion pairs linked together by two molecules of lithium chloride. The two halves of the molecule are related by a crystallographic twofold rotation axis.

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## Comment

The synthesis and structural characterization of imido analogues of oxo-anions of *p*-block elements is an area which has grown significantly over recent years (Brask & Chivers, 2001). However, taking into consideration the huge number of naturally occurring oxo-anions of silicon and their structural diversity (Greenwood & Earnshaw, 1984), relatively few examples of the isoelectronic imido analogues are known.



Synthesis of a range of imido silicate anions may be expected from the sequential deprotonation reactions of a neutral tetraamidosilane,  $\text{Si}(\text{NHR})_4$ . This route has been successfully utilized to prepare a tris(imido)amidosilicate trianion,  $[\text{Si}(\text{NR})_3(\text{NHR})]^{3-}$ , when  $R = \textit{iPr}$  (Brask *et al.*, 2000). However, it proved impossible to synthesize the corresponding tetraanion,  $[\text{Si}(\text{NR})_4]^{4-}$  ( $R = \textit{iPr}$ ), using the deprotonation method, even in the presence of excess  $\textit{nBuLi}$ . An alternative approach, using four equivalents of the dilithium salt  $\text{Li}_2\text{NR}$  ( $R = 1\text{-naphthyl}$ ) with  $\text{SiCl}_4$  was successful (Brask *et al.*, 2000); the first solid-state structure of a tetraamidosilicate tetraanion was elucidated only recently (Copsey *et al.*, 2006).

During investigations into the synthesis of novel imido anions of silicon, we found that treating the neutral tetraamidosilane  $\text{Si}(\text{NH}\textit{tBu})_4$  with two equivalents of  $\textit{nBuLi}$  produced a dilithium derivative of a bis(imido)bis(amido)-silicate dianion, isolated as the dimeric lithium chloride complex  $\{\text{Li}_2(\text{THF})_2[\text{Si}(\text{N}\textit{tBu})_2(\text{NH}\textit{tBu})_2]\cdot\text{LiCl}\}_2$ , (I). Other examples of amidosilicate dianions, which are synthesized by different routes, include  $\{\text{Li}_2[\text{Si}(\text{NH}\textit{tBu})_2(\text{NMe})_2]\}_4$  (Rakebrandt *et al.*, 1997),  $\{\text{Li}_2[\text{Si}(\text{NMe})_2(\text{N}\textit{tBu})_2]\}_2$  (Engering *et al.*, 2001) and  $\{\text{Li}_2[\text{Si}(\text{NSiMe}_3)_2(\text{NMe})_2]\}_2$  (Engering *et al.*, 2002).

Complex (I) is dimeric with the two halves of the molecule related by a twofold rotation axis. Each half of the dimer contains a distorted tetrahedral silicon centre bonded to two imido groups, each bridging two THF-solvated lithium centres. There are two further amide groups bonded to silicon. The two bis(imido)bis(amido)silicate dianions are bridged by two molecules of lithium chloride, forming a heteromolecular ladder structure (Downard & Chivers, 2001). Each lithium atom of the central  $\text{Li}_2\text{Cl}_2$  unit is coordinated by one imide and one amide nitrogen. The Li–Cl distances are similar to the corresponding lengths in the related ladder structure  $\{\text{Li}[(^t\text{Bu})\text{C}(\text{N}^t\text{Bu})_2]\}_2\cdot\text{LiCl}\cdot\text{THF}\}_2$  (Chivers *et al.*, 1999). The imido nitrogen gives the two shortest Si–N distances, at 1.704 (2) and 1.716 (2) Å, indicating some double-bond character. The amido nitrogen forms longer bonds, with Si1–N4 lengthened to 1.802 (2) Å due to the coordination of this nitrogen to the  $\text{Li}_2\text{Cl}_2$  unit. These Si–N bond lengths are comparable to those in other imido silicate anions of this type (Brask *et al.*, 2000).

## Experimental

A diethyl ether solution (10 ml) of  $\text{SiCl}_4$  (0.24 ml, 2.16 mmol) was added dropwise at 233 K to a diethyl ether solution (30 ml) of  $\text{LiN}(\text{H}^t\text{Bu})$  (0.68 g, 8.66 mmol). The reaction was warmed slowly to room temperature and stirred for 4 h.  $^t\text{BuLi}$  (3.45 ml, 2.5 M in hexanes) was added at 223 K and the reaction mixture was stirred for 16 h. Addition of tetrahydrofuran (THF; 2 ml) and filtration produced a light-brown solution. The filtrate was concentrated to 5 ml and stored at 253 K, yielding colourless needles (0.27 g, 30% yield) of (I) after several days. As the tetraamidosilane,  $\text{Si}(\text{NHR})_4$ , was not isolated from the reaction before deprotonation, lithium chloride was present in the reaction solution, resulting in incorporation in the final product. Attempts to crystallize  $\text{Li}_2[\text{Si}(\text{N}^t\text{Bu})_2(\text{NH}^t\text{Bu})_2]$ , without entrapment of LiCl, have been unsuccessful.

### Crystal data

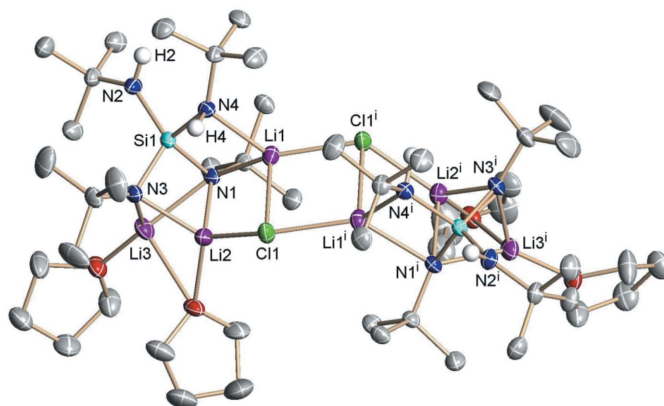
$[\text{Li}_6(\text{C}_{16}\text{H}_{38}\text{N}_4\text{Si})_2\text{Cl}_2(\text{C}_4\text{H}_8\text{O})_4]$	$Z = 4$
$M_r = 1030.14$	$D_x = 1.085 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 19.405$ (4) Å	$\mu = 0.18 \text{ mm}^{-1}$
$b = 10.632$ (2) Å	$T = 173$ (2) K
$c = 30.693$ (6) Å	Plate, colourless
$\beta = 95.40$ (3)°	$0.20 \times 0.15 \times 0.05 \text{ mm}$
$V = 6304$ (2) Å <sup>3</sup>	

### Data collection

Nonius KappaCCD diffractometer	10599 measured reflections
$\varphi$ and $\omega$ scans	5541 independent reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	3720 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.964$ , $T_{\max} = 0.991$	$R_{\text{int}} = 0.047$
	$\theta_{\max} = 25.0^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 10.6595P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{\max} = 0.008$
$S = 1.04$	$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
5541 reflections	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
355 parameters	
H-atom parameters constrained	



**Figure 1**

The molecular structure of complex (I). H atoms, except those on nitrogen, have been omitted and only one disorder component of the THF molecules is shown for clarity.

**Table 1**

Selected geometric parameters (Å, °).

Si1–N3	1.704 (2)	N3–Li3	2.004 (6)
Si1–N1	1.716 (2)	N3–Li2	2.060 (5)
Si1–N2	1.745 (2)	N4–Li1	2.094 (5)
Si1–N4	1.802 (2)	Li1–Cl1 <sup>i</sup>	2.339 (5)
N1–Li2	2.102 (5)	Li1–Cl1	2.500 (5)
N1–Li3	2.141 (6)	Cl1–Li2	2.312 (5)
N1–Li1	2.215 (5)		
N3–Si1–N1	95.48 (11)	N3–Si1–N4	110.02 (12)
N3–Si1–N2	120.12 (12)	N1–Si1–N4	106.71 (11)
N1–Si1–N2	120.69 (12)	N2–Si1–N4	103.24 (11)

Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ .

Li2 and Li3 are solvated by two molecules of THF, both of which are disordered over two positions. For the THF molecule bound to Li3, the anisotropic displacement parameters gave the best refinement with occupancy factors of 0.8 and 0.2. The second molecule of THF bridges Li2 and Li3, and the anisotropic displacement parameters gave the best refinement with occupancy factors of 0.65 and 0.35. Pairs of corresponding atoms in the two components of each ligand were assigned the same anisotropic displacement parameters. Geometric restraints were used to obtain reasonable C–O and C–C distances in one THF ligand. All H atoms, with the exception of H2 and H4, were placed in geometrically idealized positions and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$  and  $\text{C–H} = 0.98\text{--}0.99$  Å. Atoms H2 and H4 were first located in a difference map, and then refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and  $\text{N–H} = 0.88$  and  $0.93$  Å, respectively.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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