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The tetralithium derivative of the tetrakis(1-naphthylimido)silicate tetraanion

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.127
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, bis(diethyl ether-κO)tetra(tetrahydrofuran-κO)[μ_4-tetrakis(1-naphthylimido)silane(4−)]tetralithium(I) diethyl ether solvate, $[Li_4(C_{40}H_{28}N_4Si)(C_4H_8O)_4(C_4H_{10}O)_2]\cdot C_4H_{10}O$, has been structurally characterized. The compound contains the tetrakis(naphthylimido)silicate tetraanion, which is formally isoelectronic with the orthosilicate anion, $[SiO_4]^{4-}$. The two halves of the molecule are equivalent, related by a crystallographic twofold rotation axis.

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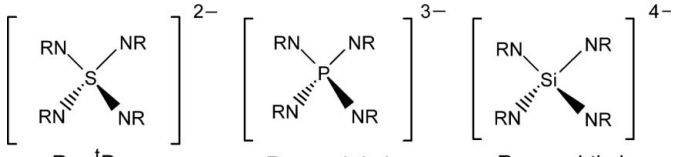
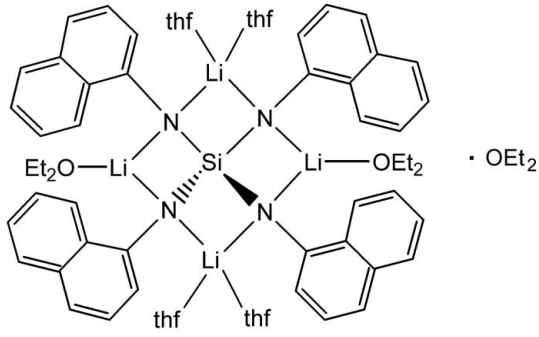
Comment

The synthesis and structural characterization of polyimido anions of p-block elements is an area which has flourished in recent years (Brask & Chivers, 2001). Two notable examples are the imido analogues of the orthosulfate dianion, (I) (Fleischer *et al.*, 1997), and the orthophosphate trianion, (II) (Raithby *et al.*, 1997; Bickley *et al.*, 2004). In 2000, the synthesis of the tetraimido silicate tetraanion, (III), as the tetralithium etherate, $[Li(OEt_2)]_4[Si(NR)_4]$ (R = 1-naphthyl) was first reported (Brask *et al.*, 2000), but no structural data could be obtained. Here, we report the first structural determination of a complex containing the tetraimidosilicate tetraanion, the title compound, (IV) (Fig. 1).



(I) (II) (III)



(IV)

Complex (IV) contains a distorted tetrahedral Si atom, bound to four imido N centres. The four imido N atoms are bridged by Li atoms to form an eight-membered Li_4N_4 ring.

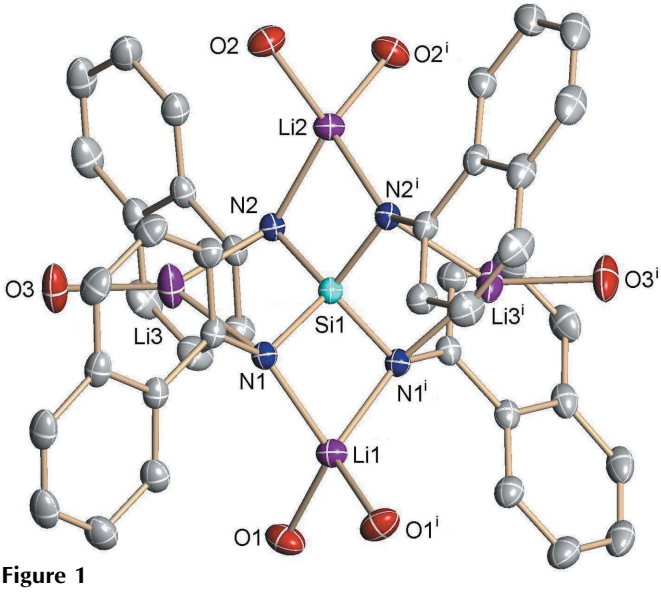


Figure 1
The molecular structure of complex (IV). Displacement ellipsoids are drawn at the 50% probability level. H atoms and the Et_2O solvent have been omitted, and only O atoms from the coordinated solvent molecules are shown, for clarity. [Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.]

Two of these atoms, Li1 and Li2, are tetrahedral, each being additionally coordinated by two molecules of tetrahydrofuran. The remaining two Li atoms, Li3 and Li3^{i} [symmetry code: (i) $-x, y, \frac{1}{2}-z$], are three-coordinate and have distorted trigonal-planar geometry, each solvated by one molecule of diethyl ether. The complex contains a further molecule of diethyl ether in the crystal structure. The Si—N bond lengths of 1.735 (2) and 1.738 (1) Å are comparable with previously reported Si–imido distances (Brask *et al.*, 2000).

For comparison, the lithium derivatives of (I) and (II) have been isolated as the neutral complex $S(N^tBu)_4[Li(thf)_2]_2$ (thf is tetrahydrofuran; Fleischer *et al.*, 1997) and the solvent-separated ion pair $[Li(thf)_4][P(NR)_4[Li(thf)_2]_2$ (Raithby *et al.*, 1997), respectively. Complex (IV) is a unique example of a tetraimidosilicate tetraanion, prepared from the reaction of $SiCl_4$ and $Li_2(NR)$. Deprotonation of $Si(NHR)_4$ is restricted to the formation of di- and tri-anions (Copsey *et al.*, 2006; Brask *et al.*, 2000).

Experimental

The synthesis of (IV) was carried out according to the literature procedure (Brask *et al.*, 2000). Single crystals for this study were grown from a concentrated solution of (IV) in tetrahydrofuran and diethyl ether (1:1) at room temperature over several days.

Crystal data

$[Li_4(C_{40}H_{28}N_4Si)(C_4H_8O)_4(C_4H_{10}O)_2]\cdot C_4H_{10}O$
M_r = 1131.29
Monoclinic, $C2/c$
a = 27.561 (6) Å
b = 14.829 (3) Å
c = 17.617 (4) Å
β = 118.38 (3)°
V = 6335 (3) Å^3
Z = 4
D_x = 1.186 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 173 (2) K
Block, yellow
0.12 × 0.09 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.992, T_{max} = 0.995
21125 measured reflections
5558 independent reflections
4207 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.128
S = 1.02
5558 reflections
408 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 4.7032P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Si1—N1	1.7352 (15)	N1—Li3	2.138 (4)
Si1—N2	1.7375 (14)	N2—Li2	2.033 (3)
N1—Li1	2.026 (4)	N2—Li3	2.100 (4)
N1—Si1—N1^{i}	100.20 (10)	O2^{i}—Li2—O2	99.1 (2)
N1—Si1—N2	108.92 (7)	O2—Li2—N2^{i}	116.99 (6)
N1^{i}—Si1—N2	120.17 (7)	O2—Li2—N2	121.90 (7)
N2—Si1—N2^{i}	99.75 (10)	N2^{i}—Li2—N2	81.60 (17)
O1^{i}—Li1—O1	100.1 (2)	O3—Li3—N2	133.52 (19)
O1—Li1—N1^{i}	115.59 (6)	O3—Li3—N1	140.9 (2)
O1—Li1—N1	122.44 (7)	N2—Li3—N1	83.65 (13)
N1^{i}—Li1—N1	82.14 (18)		

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

The solvent molecule of diethyl ether is disordered over four positions, two of which are generated by a crystallographic twofold rotation axis. The two located positions, O4/C40–C43 and O5/C50–C53, were refined with occupancy factors of 0.3 and 0.2, respectively, which gave optimal displacement parameters. The O atoms were refined anisotropically and the C atoms were refined isotropically. The pairs of C atoms, C42/C52 and C40/C53, were allowed to refine with the same isotropic displacement parameters. Geometric restraints were applied to obtain reasonable C—C and C—O distances. The H atoms were placed in geometrically idealized positions and refined as riding, with $U_{iso}(H) = 1.2–1.5U_{eq}$ (parent atom). C—H distances are in the range 0.95–0.99 Å.

Data collection: *COLLECT* (Nonius, 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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