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Tris(1-lithio-4,7-dimethyl-1,4,7-triazacyclononane)

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.058
wR factor = 0.071
Data-to-parameter ratio = 19.2

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

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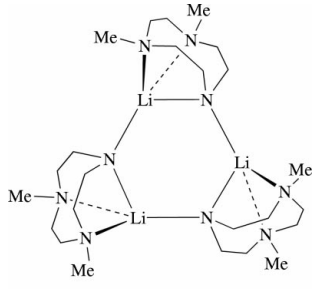
The title compound, $[Li(Me_2[9]aneN_3)]_3$ or $[Li_3(C_8H_{18}N_3)_3]$, (I), possesses a trimeric structure featuring four-coordinate N and Li atoms. Each of the Li atoms is bonded to the two amino N atoms and one amido N atom of one macrocycle, and to a further amido N atom of a second macrocycle. The central 'core' is an essentially planar Li_3N_3 ring.

Comment

We recently found that reaction of $HMe_2[9]aneN_3$ (1,4-dimethyl-1,4,7-triazacyclononane) with *n*-butyllithium in hexanes affords a mono-lithiated derivative, (I), that we formulated simply as '$[Li(Me_2[9]aneN_3)]_x$' (Fletcher *et al.*, 2000). The ^{1}H NMR spectrum of this material showed two inequivalent methyl resonances and six different ring methylene atom resonances, indicative of a polynuclear material. Unfortunately, diffraction-quality crystals were not obtained, but at around this time Giesbrecht *et al.* (2000) and Qian *et al.* (2000) independently described the X-ray crystal structure of the *N,N′*-diisopropyl analogue of (I). These dimeric molecules, $[Li(^iPr_2[9]aneN_3)]_2$, contain central $\{Li_2N_2\}$ cores with the amido N atoms bridging the two Li atoms, the coordination spheres of which are completed by the two amino N atoms of the macrocycles. We recently obtained diffraction-quality crystals of (I) and here report its X-ray structure.



(I)

Molecules of (I) adopt a trimeric structure in the solid state, possessing approximate molecular C_{3h} symmetry (Fig. 1). Each Li and each amido N atom is four-coordinate, with the Li atoms deviating most from a tetrahedral geometry. The central $\{Li_3N_3\}$ core is effectively planar with the maximum and minimum deviations from the (Li1, N9, Li2, N29, Li3 and N39) least-squares plane being *ca* 0.069 Å, and the sum of the internal angles being 717.2 (9)° (mean 119.5°). The internal N—Li—N angles [range 135.27 (17)–137.34 (17)°, mean 136.2°] are considerably larger than the internal Li—N—Li angles [range 101.75 (14)–103.68 (14)°, mean 102.6°]. The lithium—N_{amide} distances [range 1.975 (3)–2.040 (3) Å, mean 2.006 Å] are significantly shorter than the lithium—N_{amine} distances [range 2.140 (3)–2.188 (3) Å, mean 2.163 Å], as

expected. The Li—N distances and N—Li—N and Li—N—Li angles in (I) (Table 1) span the typical ranges reported for lithiated amines and amides (Fletcher *et al.*, 1996; Allen & Kennard, 1993). While both planar and puckered $\{Li_3N_3\}$ ring motifs are well known in the structural chemistry of lithium amides (Fletcher *et al.*, 1996; Allen & Kennard, 1993), compound (I) is the first to feature an $\{Li_3N_3\}$ ring in which both the N and Li atoms are classically four-coordinate.

Experimental

Tris(1-lithio-4,7-dimethyl-1,4,7-triazacyclononane) was prepared according to previously described procedures (Fletcher *et al.*, 2000). Crystallization of the crude product from pentane afforded (I) as air-sensitive colourless blocks.

Crystal data

$[Li_3(C_8H_{18}N_3)_3]$
M_r = 489.58
Monoclinic, $P2_1/c$
a = 11.8682 (2) Å
b = 11.8465 (3) Å
c = 22.1205 (4) Å
β = 103.374 (2)°
V = 3025.7 (1) Å^3
Z = 4
D_x = 1.075 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6459 reflections
θ = 2.9–27.5°
μ = 0.07 mm^{-1}
T = 150 K
Block, colourless
0.42 × 0.32 × 0.26 mm

Data collection

Enraf–Nonius Kappa CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*DENZO*; Otwinowski & Minor, 1997)
T_{min} = 0.979, T_{max} = 0.983
11 636 measured reflections
6922 independent reflections
4174 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 13$
$l = -28 \rightarrow 28$

Refinement

Refinement on F
R = 0.058
wR = 0.071
S = 1.03
6275 reflections
326 parameters
H-atom parameters constrained
Chebychev polynomial with coefficients 1.30, 1.35, 0.971, 0.203 (*CRYSTALS*; Watkin *et al.*, 2001)
$(\Delta/\sigma)_{max}$ = 0.025
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 79 (18)

Table 1
Selected geometric parameters (Å, °).

Li1—N3	2.188 (3)	Li2—N26	2.186 (3)
Li1—N6	2.142 (3)	Li2—N29	2.026 (3)
Li1—N9	2.030 (3)	Li3—N29	1.988 (3)
Li1—N39	1.977 (3)	Li3—N33	2.140 (3)
Li2—N9	1.975 (3)	Li3—N36	2.182 (4)
Li2—N23	2.141 (3)	Li3—N39	2.040 (3)
N3—Li1—N6	84.54 (12)	N26—Li2—N29	88.11 (13)
N3—Li1—N9	87.55 (13)	N29—Li3—N33	120.11 (16)
N6—Li1—N9	88.20 (13)	N29—Li3—N36	124.31 (17)
N3—Li1—N39	123.23 (16)	N33—Li3—N36	84.76 (13)
N6—Li1—N39	120.49 (16)	N29—Li3—N39	136.02 (18)
N9—Li1—N39	137.34 (17)	N33—Li3—N39	89.00 (13)
N9—Li2—N23	121.16 (16)	N36—Li3—N39	87.70 (13)
N9—Li2—N26	124.21 (15)	Li1—N9—Li2	103.14 (14)
N23—Li2—N26	84.36 (12)	Li2—N29—Li3	103.68 (14)
N9—Li2—N29	135.27 (17)	Li1—N39—Li3	101.75 (14)
N23—Li2—N29	88.82 (13)		

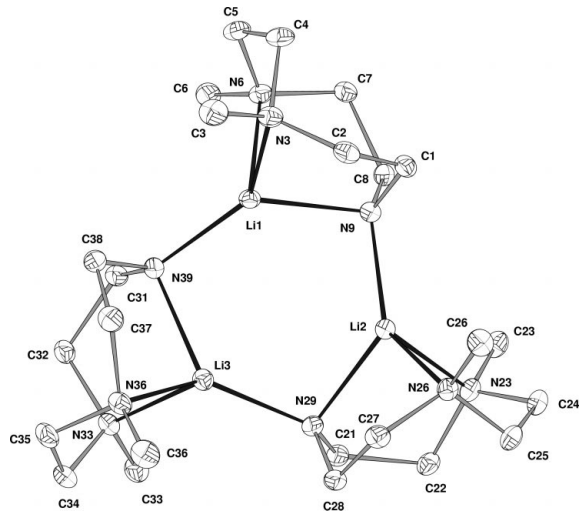


Figure 1
View of the molecular structure of (I), approximately perpendicular to the $\{Li_3N_3\}$ ring least-squares plane. Displacement ellipsoids are drawn at the 25% probability level and H atoms have been omitted for clarity.

All H atoms were placed geometrically. Six low-angle reflections (112, $\bar{1}22$, $\bar{2}11$, $\bar{2}12$, 022, $\bar{1}04$) with severely underestimated $|F_o|$ were omitted from refinement cycles. Otherwise refinement was carried out against 6275 data with $I > 0$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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