

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (III)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ti1	0.20585 (9)	0.32310 (8)	0.13327 (5)	0.01949 (18)
Cl1	0.46430 (14)	0.39575 (11)	0.22445 (7)	0.0299 (3)
Cl2	0.15040 (14)	0.11212 (11)	0.16810 (7)	0.0264 (3)
Cl3	0.29291 (13)	0.51583 (10)	0.07747 (6)	0.0246 (2)
Cl4	-0.04572 (13)	0.25393 (11)	0.03555 (6)	0.0251 (2)
Cl5	0.06205 (14)	0.44744 (11)	0.24240 (7)	0.0300 (3)
N11	0.3307 (4)	0.2026 (3)	0.0272 (2)	0.0196 (8)
Cl2	0.2522 (5)	0.0907 (4)	-0.0405 (3)	0.0213 (9)
N13	0.3665 (4)	0.0386 (3)	-0.0942 (2)	0.0216 (8)
Cl3	0.3261 (6)	-0.0848 (5)	-0.1748 (3)	0.0315 (11)
Cl4	0.5265 (5)	0.1218 (5)	-0.0591 (3)	0.0266 (10)
Cl5	0.5043 (5)	0.2222 (4)	0.0153 (3)	0.0244 (10)
N21	0.7180 (5)	0.6515 (4)	0.1425 (2)	0.0345 (9)
C22	0.8874 (6)	0.6663 (4)	0.1409 (3)	0.0282 (10)
N23	0.9651 (4)	0.7598 (3)	0.2165 (2)	0.0219 (8)
C23	1.1510 (5)	0.8059 (5)	0.2407 (3)	0.0326 (11)
C24	0.8412 (6)	0.8036 (5)	0.2688 (3)	0.0332 (11)
C25	0.6864 (6)	0.7357 (5)	0.2223 (3)	0.0369 (12)
N31	0.3057 (5)	0.5901 (4)	0.5267 (3)	0.0396 (10)
C32	0.2710 (6)	0.4826 (5)	0.4514 (3)	0.0347 (11)
N33	0.1718 (5)	0.3729 (4)	0.4654 (2)	0.0299 (9)
C33	0.1040 (7)	0.2320 (5)	0.3993 (3)	0.0437 (13)
C34	0.1432 (6)	0.4129 (5)	0.5521 (3)	0.0343 (12)
C35	0.2276 (6)	0.5487 (5)	0.5901 (3)	0.0375 (12)
Ti2	1/2	1	1/2	0.0268 (3)
Cl21	0.49886 (15)	1.07407 (13)	0.37399 (7)	0.0359 (3)
Cl22	0.19956 (14)	0.93235 (14)	0.47824 (8)	0.0412 (3)
Cl23	0.52107 (17)	0.76923 (13)	0.41544 (8)	0.0422 (3)

Table 6. Selected geometric parameters (\AA , $^\circ$) for (III)

Ti1—N11	2.167 (3)	Ti1—Cl3	2.3767 (12)
Ti1—Cl1	2.3043 (13)	Ti2—Cl22	2.3297 (11)
Ti1—Cl5	2.3055 (12)	Ti2—Cl23	2.3323 (11)
Ti1—Cl4	2.3164 (12)	Ti2—Cl21	2.3523 (10)
Ti1—Cl2	2.3164 (12)		
N11—Ti1—Cl1	90.26 (9)	Cl5—Ti1—Cl2	94.78 (4)
N11—Ti1—Cl5	177.59 (10)	Cl4—Ti1—Cl2	91.59 (4)
Cl1—Ti1—Cl5	92.14 (5)	N11—Ti1—Cl3	84.28 (9)
N11—Ti1—Cl4	87.59 (9)	Cl1—Ti1—Cl3	88.38 (4)
Cl1—Ti1—Cl4	176.73 (5)	Cl5—Ti1—Cl3	95.98 (4)
Cl5—Ti1—Cl4	90.02 (4)	Cl4—Ti1—Cl3	88.96 (4)
N11—Ti1—Cl2	84.99 (9)	Cl2—Ti1—Cl3	169.22 (5)
Cl1—Ti1—Cl2	90.68 (4)		
Cl1—Ti1—N11—Cl2	155.7 (3)	Cl2—Ti1—N11—Cl2	65.1 (3)
Cl4—Ti1—N11—Cl2	-26.7 (3)	Cl3—Ti1—N11—Cl2	-115.9 (3)

The data collection nominally covered a sphere of reciprocal space by a combination of seven, for (I) and (II), and six, for (III), sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was complete to at least 26.4° in θ , for (I) and (II), and 90% complete to at least 24.7° in θ , for (III). Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms were located by difference Fourier synthesis and the H atoms bonded to carbon were refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{eq}(\text{C})$, $U(\text{H}) = 1.2U_{eq}(\text{C})$ or $U(\text{H}) = 1.2U_{eq}(\text{N})$] using a riding model with C—H(aromatic) = 0.95, C—H(methyl) = 0.98 or N—H = 0.88 \AA , respectively. The methyl group of (II) is disordered; two different positions rotated from each other by 60° were found. These two conformations were refined with the same site-occupation factor. The methyl groups of the imidazole rings of (III) were allowed to rotate about their local threefold axis.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1252). Services for accessing these data are described at the back of the journal.

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catena-Poly[[bis(μ -2,6-dimethylpiperidino-*N:N*)dilithium]- μ -(*N,N,N',N'*-tetramethylethylenediamine-*N:N'*)]

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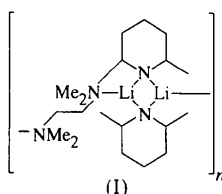
Abstract

The title compound, $[\text{Li}_2(\text{C}_7\text{H}_{14}\text{N})_2(\text{C}_6\text{H}_{16}\text{N}_2)]_n$, is a chain polymer in which strictly planar Li_2N_2 rings incorporating 2,6-dimethylpiperidino ligands are linked by

N,N,N',N'-tetramethylethylenediamine ligands in a rare bridging role. The Li atom is planar three-coordinate. The internal ring angles are obtuse [107.89(11)°] at lithium and acute [72.11(11)°] at nitrogen, as is commonly found for lithium amide ring structures.

Comment

The title compound, (I), together with other related lithium amides, was prepared in order to study its efficacy as an initiator of the polymerization of methyl methacrylate (Couper *et al.*, 1998). Complexes prepared in tetrahydrofuran, and with the addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), proved to be effective as such initiators. The crystal structure of the title compound was determined as part of its full characterization.



In the crystalline solid state, compound (I) is polymeric, with TMEDA ligands linking dimeric Li₂N₂ rings containing the substituted piperidinido ligands to give chains (Fig. 1). The Li₂N₂ rings are centrosymmetric and hence strictly planar, with obtuse internal angles at the three-coordinate Li atoms and acute internal angles at the four-coordinate N atoms, as is normal

in lithium amide ring systems. The two discrete Li—N bond lengths within the ring are only slightly different [2.038(3) and 2.050(3) Å], and are shorter than the dative Li—N bonds [2.161(2) Å] formed with the bridging TMEDA ligands. The piperidine rings have the expected chair conformation, with both methyl substituents in equatorial positions.

The TMEDA bridging ligand has a fully extended conformation, with a 180° N—C—C—N torsion angle imposed by centrosymmetry at the midpoint of the C—C bond. The TMEDA ligand rarely functions as a bridging ligand, and is far more commonly found in a chelating role, with both N atoms bonded to the same metal atom. A search of the Cambridge Structural Database (Allen & Kennard, 1993) yielded only 22 different structures with bridging TMEDA. Of these, about half are dinuclear complexes of Al or Ga (there is one polymeric Al complex; Palenik, 1964); there is one complex each for Mo (polymeric; Kerby *et al.*, 1990), Zn (dimeric; Malik *et al.*, 1997) and Sn (dimeric; Braunschweig *et al.*, 1995). Nine structures are of Li complexes, and there are none with other alkali metals. Of these nine Li complexes, only one is a lithium amide (Bernstein *et al.*, 1992), derived from the widely used synthetic reagent lithium diisopropylamide (LDA), itself a helical chain polymer (Barnett *et al.*, 1991), by complexation with TMEDA. In its essential features, this closely resembles the current structure; the main difference is a considerably smaller Li—N—CH₂ angle at the ligand bridge for the LDA complex, by almost 8°, which is presumably a consequence of the difference in steric requirements of the diisopropylamido and 2,6-dimethylpiperidinido ligands.

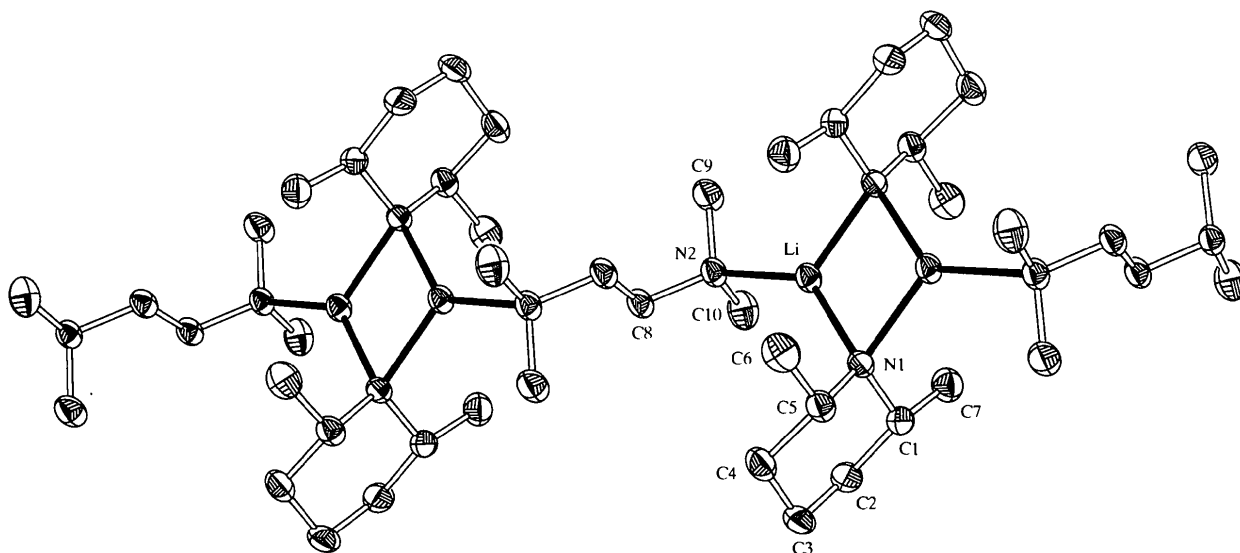


Fig. 1. A segment of the polymeric chain structure of the title compound, with unique atom labels and 50% probability ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was prepared as described by Couper *et al.* (1998). Suitable crystals were obtained directly from the synthesis; they were relatively large and could not be cut without causing damage which resulted in a deterioration of the diffraction pattern.

Crystal data

[Li₂(C₇H₁₄N)₂(C₆H₁₆N₂)]

$M_r = 354.47$

Triclinic

$P\bar{1}$

$a = 7.904$ (5) Å

$b = 8.899$ (6) Å

$c = 9.335$ (7) Å

$\alpha = 108.26$ (4)°

$\beta = 112.63$ (3)°

$\gamma = 91.41$ (3)°

$V = 567.6$ (7) Å³

$Z = 1$

$D_x = 1.037$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 30

reflections

$\theta = 8.5$ – 12.0 °

$\mu = 0.060$ mm⁻¹

$T = 160$ (2) K

Block

$1.15 \times 0.85 \times 0.65$ mm

Colourless

Data collection

Stoe–Siemens diffractometer

with Cryostream cooler

(Cosier & Glazer, 1986)

ω/θ scans

Absorption correction: none

4012 measured reflections

2004 independent reflections

1631 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 24.99$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

5 standard reflections

frequency: 60 min

intensity decay: 2.9%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.109$

$S = 1.027$

2004 reflections

122 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.1264P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.199$ e Å⁻³

$\Delta\rho_{min} = -0.181$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Li—N1	2.038 (3)	Li—N2	2.161 (2)
Li—N1 ⁱ	2.050 (3)		
N1—Li—N1 ⁱ	107.89 (11)	Li—N1—Li ⁱ	72.11 (11)
N1—Li—N2	133.67 (11)	C8—N2—Li	122.92 (10)
N1 ⁱ —Li—N2	118.15 (11)	N2—C8—C8 ⁱⁱ	113.35 (13)
C1—N1—C5	106.17 (11)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$.

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to

solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1078). Services for accessing these data are described at the back of the journal.

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Dichlorobis(2-hydroxymethyl-1-methylimidazole-*N*³)zinc(II)

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Abstract

The crystal structure of the title complex, [ZnCl₂(C₅H₈N₂O)₂], is composed of discrete molecules. The Zn^{II} atom is coordinated by two chloride ligands and two N atoms from the imidazole ligands in a distorted tetrahedral coordination environment, with Zn—N distances of