

(1*R*,2*R*)-(-)-Bis[μ_4 -1-{[1,1-dimethyl-2-(trimethylsilyl)amidino]amino}-2-({1,1-dimethyl-2-[1,1-dimethyl-2-(trimethylsilyl)amidino]amidino}amino)-cyclohexane}]tetralithium(I)

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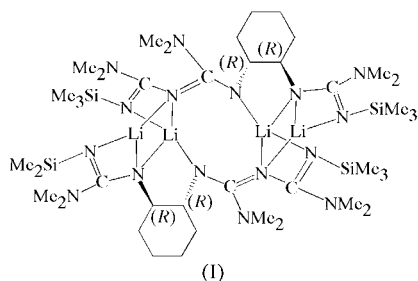
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The title compound, $[\text{Li}_4(\text{C}_{21}\text{H}_{46}\text{N}_8\text{Si}_2)_2]$, has been prepared and its structure determined. The whole molecule can be regarded as a molecular cage made up of the central eight-membered ring and six contiguous rings of three types. As the first example of a bridged amidinate–dicyanamide framework, this noteworthy structure and its electronic features are presented.

Comment

The amidinate ligand remains a noteworthy group for incorporation into a wide variety of transition and main-group metal complexes, as its steric and electronic effects can be manipulated through programmed variation of the substituents (Barker & Kilner, 1994; Edelmann, 1994). The addition reaction of nitrogen anions as nucleophiles with nitriles has been proved to be a useful and popular method to obtain this kind of ligand (Bambirra *et al.*, 2001; Sanger, 1973). In our previous publications (Li *et al.*, 2002*a,b*), we reported varied



benzamidinates templated by $[(1*R*,2*R*)-(-)-1,2-(\text{NHSiMe}_3)_2\text{-C}_6\text{H}_{10}]$ and studied their structures formally (Li *et al.*, 2003). In order to conduct a thorough investigation, a novel reaction with non-aromatic dimethylcyanamide as substrate was successfully developed, yielding the title compound, (I), and the results are reported here.

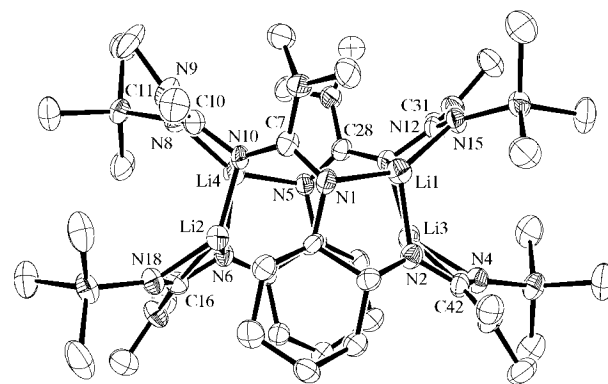


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Treatment of $\text{Li}_2[(1*R*,2*R*)-(-)-1,2-(\text{NSiMe}_3)_2\text{-C}_6\text{H}_{10}]$ with two molar equivalents of $(\text{Me})_2\text{NCN}$ gave a crystalline product, (I). It was initially assumed that a typical double-addition reaction had occurred and given a bridged bis-(amidinate) compound, through the mechanism reported by Li *et al.* (2002). However, spectroscopic characterization of (I) reveals an unexpected η^3, η^5 dianion, which results from single and double 1,3-migration of the SiMe_3 group at the two tails of the dicyanocyclohexane. To our knowledge, this is the first example of a bridged amidinate–dicyanamide framework. The presence of the dicyanamide moiety as an η^5 anion is interesting, as it has been shown to be a remarkably versatile building block for the construction of supramolecular architectures, since it may act in a mono-, bi- or tridentate manner (Manson *et al.*, 1999; Batten *et al.*, 1998).

The geometric parameters of (I) are listed in Table 1 and its molecular structure is illustrated in Fig. 1. Dimeric aggregation is revealed with a rigorous non-crystallographic C_2 symmetry. The central eight-membered $\text{Li1/N1/C7/N10/Li4/N5/C28/N12}$ ring shows a distorted boat–boat conformation and is made up of two dicyanamide fragments, joined to which are three other types of rings, namely two cyclohexane groups in chair conformations, two five-membered envelope rings (C1/C6/N1/Li1/N2 and C27/C22/N6/Li4/N5) and two rhombus (LiN_2) rings (Li4/N6/Li2/N10 and Li1/N12/Li3/N2). These six contiguous rings, together with the large central ring, result in the whole molecule forming a molecular cage, with a diameter ranging from 4.595 ($\text{Li1}\cdots\text{Li4}$) to 3.862 Å ($\text{C7}\cdots\text{C28}$) (Fig. 2).

It should be noted that the Li atoms (Li1 and Li4) on the central ring are four-coordinate and bridging, and the other two (Li2 and Li3) are three-coordinate. The two amidinate angles of $\text{N2}-\text{C42}-\text{N4}$ [$116.8(6)^\circ$] and $\text{N18}-\text{C16}-\text{N6}$ [$116.3(6)^\circ$] are similar to the same angles in the dicyanamide fragments bonded to the Li atoms [$\text{N12}-\text{C31}-\text{N15} = 115.1(6)^\circ$ and $\text{N10}-\text{C10}-\text{N8} = 117.0(6)^\circ$], and they are both substantially narrower than in the remaining dicyanamide $\text{N}-\text{C}-\text{N}$ moieties [$\text{N5}-\text{C28}-\text{N12} = 124.5(6)^\circ$ and $\text{N1}-\text{C7}-\text{N10} = 124.0(6)^\circ$]. In addition, the dihedral angles between the two $\text{N}-\text{C}-\text{N}$ fragments in the dicyanamide anions are

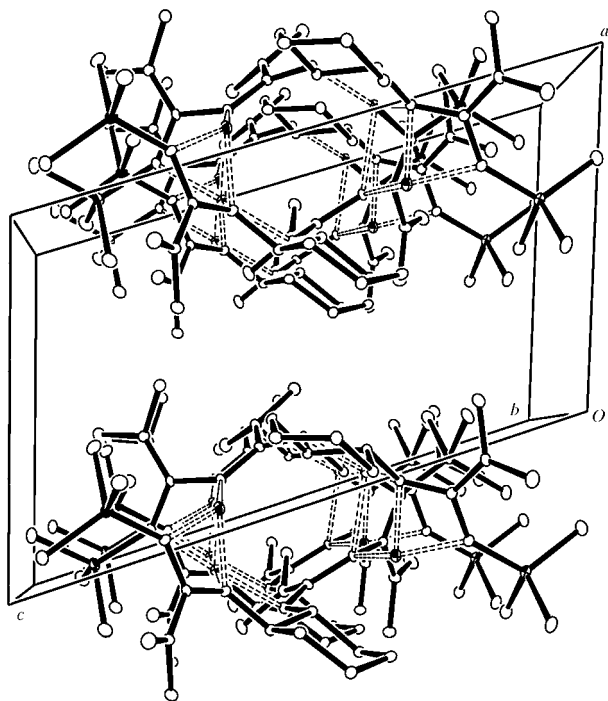


Figure 2

A packing diagram for (I), viewed along the *b* axis. All H atoms have been omitted for clarity. All Li–N bonds are shown as dashed lines to distinguish them from the covalent bonds.

similar, at 126.2° (N12–C31–N15 and N5–C28–N12) and 126.9° (N10–C10–N8 and N1–C7–N10).

A study of the bond distances in (I) gives a detailed comprehension of its structure and electronic features. It is observed that the C–N bonds in both amidinate and dicyanamide fragments [for example, C16–N18 = 1.328 (9) Å and C31–N15 = 1.322 (8) Å] are shorter than a standard C–N single bond [Lide (1962) pointed out that the standard C–N single- and double-bond lengths are 1.474 and 1.265 Å, respectively] and range from 1.308 (8) to 1.399 (8) Å, indicating some degree of π -electron delocalization in the η^3, η^5 anions. Meanwhile, the C–N(Me)₂ bonds [for example, C16–N7 = 1.367 (8) Å] are also short, in the range 1.355 (9)–1.401 (8) Å, which is interpreted in terms of π – π conjugation between the lone pairs of electrons on the N atoms and anions. These two kinds of C–N bonds are both intermediate between the standard C–N single- and double-bond distances and this is clearly shown in the following sequence: C=N (standard) < C–N (π -delocalization in η^3, η^5 anions) < C–N(Me)₂ (π – π conjugation) < C–N (standard).

Experimental

Me₂NCN (0.233 ml, 2.88 mmol) was added by syringe to a solution of the dilithium salt Li₂[(1*R*,2*R*)-(–)-1,2-(NSiMe₃)₂-C₆H₁₀] (0.39 g, 1.44 mmol) in hexane (*ca* 25 ml) at 273 K. The mixture was warmed slowly to ambient temperature and stirred for a further 12 h. After filtration and vacuum evaporation, the reaction afforded a colourless crystalline product, (I), in moderate yield (0.213 g, 44.5%).

Crystal data

[Li₄(C₂₁H₄₆N₈Si₂)₂]
M_r = 961.44
 Triclinic, *P*1
a = 9.4773 (16) Å
b = 10.8506 (19) Å
c = 15.437 (3) Å
 α = 100.075 (2)°
 β = 104.700 (2)°
 γ = 105.896 (2)°
V = 1424.9 (4) Å³

Z = 1
D_x = 1.12 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 3715 reflections
 θ = 2.4–25.9°
 μ = 0.15 mm^{–1}
T = 190 (2) K
 Block, colourless
 0.2 × 0.2 × 0.1 mm

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

*T*_{min} = 0.971, *T*_{max} = 0.985

6983 measured reflections

5017 independent reflections

5429 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.035

θ _{max} = 25°

h = –11 → 9

k = –12 → 12

l = –18 → 18

Intensity decay: 3.9%

Refinement

Refinement on *F*²

R(*F*) = 0.066

wR(*F*²) = 0.156

S = 1.14

5898 reflections

619 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 3.2074P]$

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

(Δ/σ)_{max} = 0.005

$\Delta\rho$ _{max} = 0.42 e Å^{–3}

$\Delta\rho$ _{min} = –0.40 e Å^{–3}

Table 1

Selected geometric parameters (Å, °).

Li1–N2	2.007 (12)	Li3–N12	1.980 (12)
Li1–N1	2.013 (13)	Li3–N2	2.023 (14)
Li1–N15	2.064 (13)	Li4–N5	2.017 (13)
Li1–N12	2.273 (13)	Li4–N6	2.025 (12)
Li2–N18	1.947 (12)	Li4–N8	2.056 (13)
Li2–N10	1.992 (12)	Li4–N10	2.292 (13)
Li2–N6	2.018 (14)	N7–C16	1.367 (8)
Li3–N4	1.973 (12)		
N1–C7–N10	124.0 (6)	N5–C28–N12	124.5 (6)
N8–C10–N10	117.0 (6)	N15–C31–N12	115.1 (6)
N18–C16–N6	116.3 (6)	N4–C42–N2	116.8 (6)
C1–N2–C42–N4	145.6 (6)		

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C–H distances of 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C), but each group was allowed to rotate freely about its C–C bond. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.95–1.00 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The Friedel pairs were merged in the refinement. The determination of the absolute configuration was possible from the known *R,R* configuration of the initial lithium salt (Li *et al.*, 2002*a*). Furthermore, the Flack parameter (Flack, 1983) of the compound [(1*R*,2*R*)-(–)-1,2-(NSiMe₃)₂-C₆H₁₀]₂Zr, derived from the same initial lithium salt, has been determined as 0.03 (6) (Li *et al.*, 2002*a*).

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1235). Services for accessing these data are described at the back of the journal.

References

- Bambirra, S., Meetsma, A., Hessen, B. & Teuben, J. H. (2001). *Organo-metallics*, **20**, 782–785.
- Barker, J. & Kilner, M. (1994). *Coord. Chem. Rev.* **133**, 219–300.
- Batten, S. R., Jensen, P., Moubaraki, B., Murray, K. S. & Robson, R. (1998). *Chem. Commun.* pp. 439–440.
- Edelmann, F. T. (1994). *Coord. Chem. Rev.* **137**, 403–481.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Li, J.-F., Huang, S.-P., Weng, L.-H. & Liu, D.-S. (2003). *Eur. J. Inorg. Chem.* pp. 810–813.
- Li, J.-F., Weng, L.-H., Huang, S.-P., Tong, H.-B. & Liu, D.-S. (2002a). *Acta Cryst.* **E58**, m510–m512.
- Li, J.-F., Weng, L.-H., Huang, S.-P., Tong, H.-B. & Liu, D.-S. (2002b). *Acta Cryst.* **E58**, o1078–o1080.
- Li, J.-F., Weng, L.-H., Wei, X.-H. & Liu, D.-S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1401–1405.
- Lide, D. R. Jr (1962). *Tetrahedron*, **17**, 125–134.
- Manson, J. L., Arif, A. M. & Miller, J. S. (1999). *J. Mater. Chem.* **9**, 979–983.
- Sanger, A. R. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 351–354.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.