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Bis(12-crown-4)lithium(I) bis[(*N*,*N*-diisopropylamino)borohydride(1−)]lithium(I)

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The structure of the title compound, $[Li(C_8H_{16}O_4)_2]$-$[Li(C_6H_{17}BN)_2]$, is composed of bis[(*N*,*N*-diisopropylamino)borohydride(1−)]lithium(I) anions and Li^+ cations which are eight-coordinated by two 12-crown-4 ether molecules.

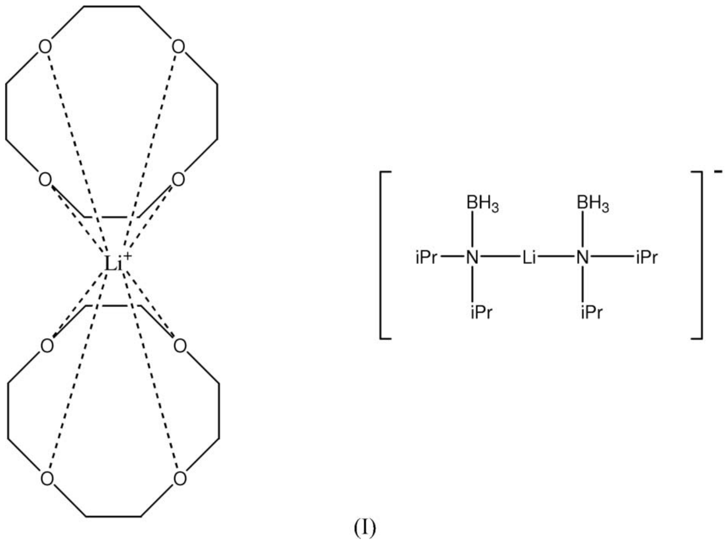
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.007 Å
R factor = 0.084
wR factor = 0.176
Data-to-parameter ratio = 19.5

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

Comment

The title compound, (I), is a well known hydride transfer reagent with advantageous properties for applications in synthetic organic chemistry (Fisher *et al.*, 1994; Thomas *et al.*, 2001; Pasumansky *et al.*, 2005). In contrast to the often used $LiAlH_4$, which shows comparable hydride transfer activity, it is not pyrophoric, is thermally stable and does not react violently with protic solvents. Lithium aminoborohydrides are readily available through deprotonation of primary or secondary amine borane adducts with *n*-butyllithium. The structures of various solvates of lithium (*N*,*N*-dimethyl)aminoborohydride, which is the methyl derivative of the title compound, have been published (Nöth *et al.*, 1996). We report here the crystal structure of the 12-crown-4 adduct (I) of $LiN^iPr_2BH_3$ along with ^1H and ^7Li NMR data.



(I)

A perspective view of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database; Version 5.27, November 2005 updated August 2006; Mogul Version 1.1; Allen, 2002). Compound (I) contains bis[(*N*,*N*-diisopropyl)aminoborohydride]lithium anions and lithium cations, which are coordinated by two 12-crown-4 molecules. Whereas one Li cation is bonded to only two N atoms (Table 1), the other is coordinated by eight O atoms of

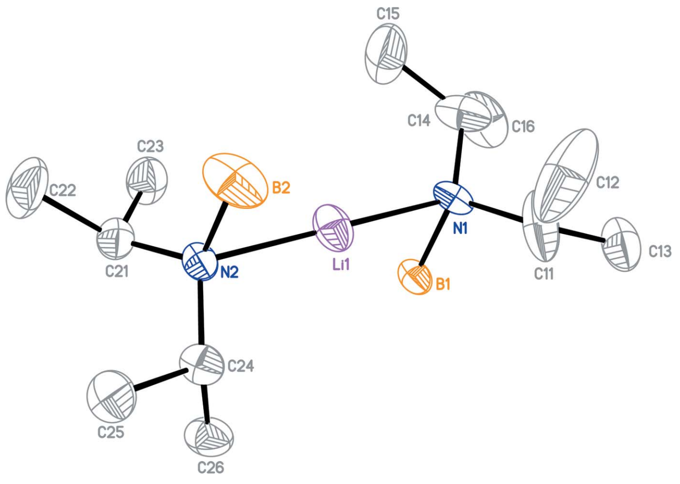


Figure 1
The anion of (I) showing displacement ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

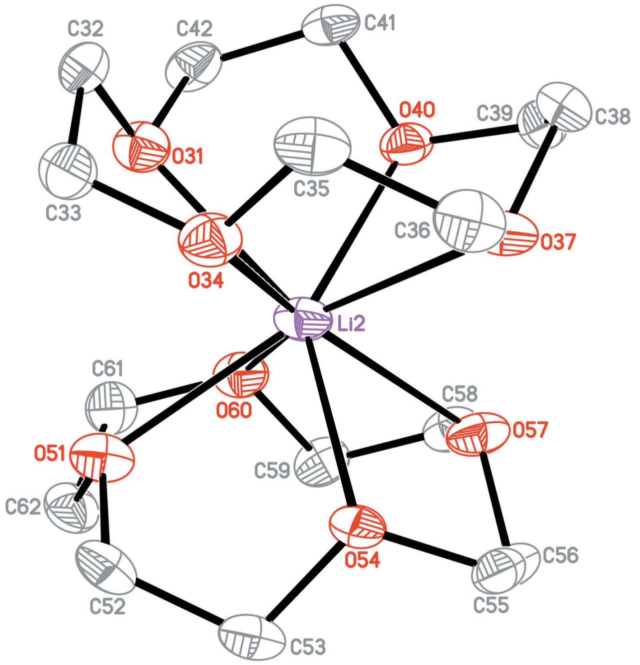


Figure 2
The cation of (I) showing displacement ellipsoids at the 50% probability level; H atoms have been omitted for clarity.

the crown ether molecules with Li—O distances ranging from 2.317 (6) to 2.475 (7) Å.

Experimental

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (THF, diethyl ether, C_6D_6) prior to use. $LiN^iPr_2BH_3$, was obtained following a literature procedure (Fisher *et al.*, 1994; Thomas *et al.*, 2001; Pasumansky *et al.*, 2005). The 12-crown-4 adduct (I) was obtained by adding an equimolar amount of crown ether to a THF solution of $LiN^iPr_2BH_3$ at room temperature. X-ray quality crystals were grown by slow cooling of a solution of (I) in THF/diethyl ether (1:3).

Crystal data

$[Li(C_8H_{16}O_4)_2][Li(C_6H_{17}BN)_2]$
$M_r = 594.33$
Triclinic, $P\bar{1}$
$a = 10.2918$ (12) Å
$b = 14.5424$ (14) Å
$c = 14.8057$ (13) Å
$\alpha = 116.790$ (7)°
$\beta = 105.314$ (8)°
$\gamma = 94.850$ (9)°
$V = 1853.7$ (4) Å^3
$Z = 2$
$D_x = 1.065$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.24 × 0.22 × 0.19 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: none
23964 measured reflections
7468 independent reflections
3312 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\rm max} = 26.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.084$
$wR(F^2) = 0.176$
$S = 0.95$
7468 reflections
382 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0110 (15)

Table 1
Selected geometric parameters (Å, °).

Li1—N1	2.049 (8)	Li2—O31	2.374 (6)
Li1—N2	2.053 (8)	Li2—O51	2.383 (7)
Li2—O54	2.317 (6)	Li2—O37	2.417 (7)
Li2—O34	2.338 (6)	Li2—O57	2.433 (6)
Li2—O40	2.360 (6)	Li2—O60	2.475 (7)
N1—Li1—N2	176.4 (4)		

H atoms were positioned geometrically (C—H = 0.98–1.00 Å, B—H = 0.98 Å) and refined as riding with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(methyl C,B)]. The BH_3 groups were allowed to rotate but not to tip.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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