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Refinement of lithium tetrahydroxoborate with low-temperature CCD data

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(O–B) = 0.001 Å
R factor = 0.029
wR factor = 0.069
Data-to-parameter ratio = 12.8

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

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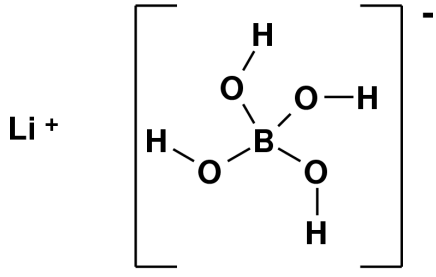
Refinement of the title compound, Li $B(OH)_4$, with CCD data at 120 K has led to a sevenfold increase in precision over the previously reported structure based on film data. The H atoms have been located and refined. Both Li and B are tetrahedrally coordinated. B—O distances are in the range 1.4644 (14)–1.4989 (13) Å, while Li—O distances are in the range 1.931 (2)–2.022 (2) Å.

Comment

While attempting to prepare RhH_2(et,ph-P4) from $RhCl_2$(et,ph-P4) [where (et,ph-P4) is $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)CH_2CH_2PEt_2$] using 'super hydride' $LiBH(C_2H_5)_3$, we encountered crystals of the title compound (I) as a byproduct, and determined its structure to ascertain its identity.



(I)

The room-temperature structure was previously reported, based on intensities from Weissenberg films, by Höhne (1964, 1966) and coworkers (Kutschabsky & Höhne, 1965; Kutschabsky & Reck, 1966). Our results confirm the published structure, with an approximate sevenfold increase in precision. Höhne's assigned H-atom positions, assigned from difference maps, lie 0.17–0.38 Å from our refined H-atom positions. Höhne's range of B—O distances, 1.472 (8) to 1.498 (8) Å, and range of Li—O distances, 1.929 (16) to 2.015 (16) Å, are in good agreement with our results (see *Abstract*).

Although all four hydrogen bonds are nearly linear, some short intermolecular contacts exist between H atoms of hydrogen-bonded OH groups. The shortest of these is 2.06 (2) Å [H1···H3(x-1/2, y, 3/2-z)]. Short intramolecular O—H···O interactions also exist within the $B(OH)_4^-$ ion. All four OH H atoms are approximately eclipsed (B—O—H···O torsion angles < 30°) with an adjacent OH, and O···H distances are in the range 2.23 (2)–2.51 (2) Å. The O—H···O angles for these contacts are in the range 73 (2)–85 (2)°.

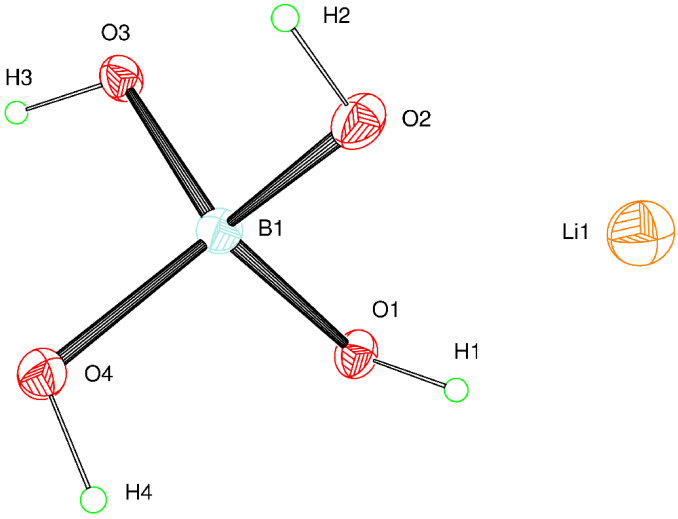


Figure 1
View of the title compound showing numbering scheme with ellipsoids drawn at the 50% level.

Experimental

A 1.0 *M* solution of $LiBH(C_2H_5)_3$ in tetrahydrofuran (0.8 ml, 0.8 mmol) was added dropwise to a rapidly stirring 1 ml methanol solution containing $RhCl_2$ (et,ph-P4) (0.5 g, 0.784 mmol) and allowed to react for 24 h. A 1 ml sample of this dark-red solution was allowed to remain undisturbed in an NMR tube for approximately 30 days, which allowed slow solvent evaporation and the formation of colorless crystals of lithium tetrahydroxoborate.

Crystal data

$Li^+ \cdot BO_4H_4^-$
M_r = 85.78
Orthorhombic, *Pbca*
a = 7.9362 (3) Å
b = 8.5220 (3) Å
c = 9.1762 (4) Å
V = 620.61 (4) Å^3
Z = 8
D_x = 1.836 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1047 reflections
θ = 2.5–30.0°
μ = 0.18 mm^{-1}
T = 120 K
Octahedron, colorless
0.20 × 0.18 × 0.17 mm
Crystal source: local laboratory

Data collection

KappaCCD diffractometer (with Oxford Cryostream)
ω scans with κ offsets
Absorption correction: none
6073 measured reflections
907 independent reflections
787 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 30.0°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.069
S = 1.11
907 reflections
71 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.3132P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Li1—O1^{i}	1.966 (2)	B1—O1	1.4774 (13)
Li1—O2	1.931 (2)	B1—O2	1.4745 (14)
Li1—O3^{ii}	1.933 (2)	B1—O3	1.4644 (14)
Li1—O4^{iii}	2.022 (2)	B1—O4	1.4989 (13)
O2—Li1—O3^{ii}	112.95 (10)	O3—B1—O2	109.18 (8)
O2—Li1—O1^{i}	123.10 (10)	O3—B1—O1	112.77 (9)
O3^{ii}—Li1—O1^{i}	104.01 (9)	O2—B1—O1	106.30 (8)
O2—Li1—O4^{iii}	98.98 (9)	O3—B1—O4	106.83 (8)
O3^{ii}—Li1—O4^{iii}	110.53 (10)	O2—B1—O4	112.89 (9)
O1^{i}—Li1—O4^{iii}	106.85 (9)	O1—B1—O4	108.97 (8)

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.807 (18)	1.990 (18)	2.7835 (11)	167.4 (16)
O2—H2···O3^{ii}	0.837 (19)	2.03 (2)	2.8643 (11)	173.4 (18)
O3—H3···O1^{iii}	0.793 (18)	1.919 (19)	2.7117 (11)	177.4 (18)
O4—H4···O2^{iv}	0.845 (18)	2.308 (18)	3.1522 (11)	178.6 (16)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{1}{2}+x, y, \frac{3}{2}-z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

H atoms were located from difference maps, and were refined individually. O—H distances were in the range 0.793 (18)–0.845 (18) Å; U_{iso} values for H atoms are in the range 0.027 (4)–0.038 (5) Å^2.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: Direct methods (*SIR*97; Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Höhne, E. (1964). *Z. Chem.* **4**, 431–432.
Höhne, E. (1966). *Z. Anorg. Allg. Chem.* **342**, 188–194.
Kutschabsky, L. & Höhne, E. (1965). *Acta Cryst.* **19**, 747–750.
Kutschabsky, L. & Reck, G. (1966). *Monatsber. Dtsch. Akad. Wiss. Berlin*, **8**, 648–654.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. (1997). *SHELXL*97. University of Göttingen, Germany.