C(37)	−0.2456 (6)	0.4002 (6)	0.4430 (5)	0.077 (8)
C(38)	−0.2271 (5)	0.2952 (6)	0.4178 (5)	0.084 (9)
C(39)	−0.1290 (5)	0.2324 (5)	0.3589 (5)	0.071 (8)
C(40)	0.1089 (4)	0.0525 (4)	0.2858 (4)	0.043 (6)
C(41)	0.1327 (7)	0.0255 (5)	0.3710 (5)	0.09 (1)
C(42)	0.1532 (7)	−0.0796 (6)	0.4028 (5)	0.11 (1)
C(43)	0.1460 (6)	−0.1574 (5)	0.3525 (5)	0.075 (9)
C(44)	0.1223 (6)	−0.1322 (5)	0.2682 (5)	0.077 (9)
C(45)	0.1030 (5)	−0.0278 (5)	0.2347 (4)	0.062 (7)
C(46)	0.0450 (5)	0.1920 (4)	0.1390 (4)	0.047 (7)
C(47)	0.1292 (6)	0.1448 (6)	0.0636 (5)	0.09 (1)
C(48)	0.1044 (8)	0.1407 (7)	−0.0214 (5)	0.11 (1)
C(49)	0.0002 (9)	0.1837 (7)	−0.0351 (5)	0.10 (1)
C(50)	−0.0832 (7)	0.2327 (8)	0.0364 (7)	0.13 (1)
C(51)	−0.0612 (6)	0.2370 (6)	0.1239 (5)	0.095 (9)

Table 2. *Selected geometric parameters (Å, °)*

Cu—S	2.367 (1)	P(1)—C(16)	1.831 (6)
Cu—Br	2.469 (1)	P(1)—C(22)	1.831 (4)
Cu—P(1)	2.279 (2)	P(1)—C(28)	1.827 (7)
Cu—P(2)	2.284 (2)	C(1)—N(1)	1.359 (8)
S—C(1)	1.691 (5)	C(1)—N(2)	1.347 (6)
N(1)—C(2)	1.411 (8)	P(2)—C(34)	1.816 (5)
N(2)—C(8)	1.474 (8)	P(2)—C(40)	1.830 (6)
N(2)—C(12)	1.477 (7)	P(2)—C(46)	1.819 (7)
S—Cu—Br	111.86 (5)	Br—Cu—P(2)	108.60 (5)
S—Cu—P(1)	111.28 (6)	N(1)—C(2)—C(3)	120.5 (6)
S—Cu—P(2)	98.01 (6)	C(1)—N(1)—C(2)	126.8 (4)
S—C(1)—N(1)	119.6 (3)	C(1)—N(2)—C(8)	119.6 (4)
S—C(1)—N(2)	121.9 (5)	C(1)—N(2)—C(12)	123.3 (4)
Cu—S—C(1)	114.0 (2)	P(1)—Cu—P(2)	124.11 (6)
Cu—P(1)—C(16)	117.5 (2)	P(1)—C(16)—C(17)	124.9 (6)
Cu—P(1)—C(22)	114.0 (2)	P(1)—C(22)—C(23)	117.5 (4)
Cu—P(1)—C(28)	113.5 (2)	P(1)—C(28)—C(29)	118.6 (5)
Cu—P(2)—C(34)	116.6 (2)	P(2)—C(34)—C(35)	119.2 (5)
Cu—P(2)—C(40)	112.9 (2)	P(2)—C(40)—C(41)	118.4 (5)
Cu—P(2)—C(46)	116.8 (2)	P(2)—C(46)—C(47)	118.7 (5)
Br—Cu—P(1)	103.08 (5)		

Table 3. *Interatomic distances (Å) and angles (°) in [Cu(PPh$_3$)$_2$(dbptH)Br], (A), [Cu(PPh$_3$)$_2$(meimtH)Br], (B), and [Cu(PPh$_3$)$_2$(py2SH)Br], (C)*

	*(A)**	*(B)*†	*(C)*‡
Cu—S	2.367 (1)	2.375 (1)	2.302 (4)
Cu—Br	2.469 (1)	2.509	2.462 (2)
Cu—P	2.279 (2)	2.281 (1)	2.263 (4)
	2.284 (2)	2.268 (1)	2.267 (4)
P—Cu—P	124.11 (6)	130.9	125.0 (2)
P—Cu—Br	103.08 (5)	106.7	104.4 (1)
	108.60 (5)	98.3	105.9 (1)
S—Cu—Br	111.86 (5)	112.6	114.9 (1)
S—Cu—P	111.28 (6)	102.9	104.5 (2)
	98.01 (6)	105.3	102.8 (2)

* Present work. † Karagiannidis *et al.* (1990). ‡ Karagiannidis *et al.* (1989).

All H atoms were calculated as riding on their C atoms at a distance of 0.95 Å, except for the amine H atom, which was calculated as riding on the N atom at a distance of 0.87 Å. Refined parameters were calculated by using anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for all H atoms.

Data collection: *CAD*-4 *MACH-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *MACH-PC Software*. Data reduction: *Xtal*3.2 *DIFDAT SORTRF ADDREF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*3.2 *SIMPEL*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lithium Tetraphenylborate.2thf.2H$_2$O

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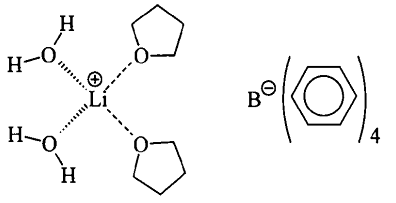
Abstract

The structure of diaquabis(tetrahydrofuran)lithium tetraphenylborate, [Li(C$_4$H$_8$O)$_2$(H$_2$O)$_2$](C$_{24}$H$_{20}$B), has been determined at 200 K. The Li$^+$ cation is coordinated by two water and two tetrahydrofuran molecules, whereas the tetraphenylborate anion does not show any contact. A crystallographic mirror plane bisects the lithium complex and the tetraphenylborate anion.

Comment

The tetraphenylborate anion is commonly used as a phase-transfer catalyst as well as a counterion in the soluble one-component Ziegler–Natta olefin polymerization catalysis (Strauss, 1993) or for hydrogen-bridged protonated amine complexes (Bock, Vaupel, Näther, Ruppert & Havlas, 1992; Bock, Vaupel, Schödel, Koch & Egert, 1994). It can be used as an effective NMR chemical-shift reagent for large cations containing organic groups, or in the quantitative analysis of metal ions and organic bases such as alkaloids and pharmaceuticals (Ibrahim, Beltagy & Rida, 1973). The negative charge is delocalized over the whole molecule and the formally negatively charged boron centre is not accessible. The only known reaction products with contacted tetraphenylborate anions (Bochmann, 1992) are η^6-coordinated transition metal complexes, in which one of the tetraphenylborate phenyl rings interacts (Fachinetti, Funaioli & Zanazzi, 1988).



(I)

For our study of the Li$^+$ coordination sphere, tetraphenylborate proved to be a suitable anion which does not interfere with the cation. The coordination sphere of the Li$^+$ cation consists of two water and two tetrahydrofuran molecules. Li1 and the two water O atoms, O1 and O2, are located on special positions (x, $\frac{3}{4}$, z). The thf molecules are related by a mirror plane. The average Li1—O distances are identical within the standard deviation (average Li—O = 1.91 Å) and are within the normal range. The coordination geometry deviates from tetrahedral: the largest difference from the tetrahedral angle of 109.3° is found for the angle between the Li$^+$ cation and the two water O centres [O1—Li1—O2 123.6 (3)°]. The angle between the two thf O centres and the Li$^+$ cation, O3—Li1—O3*A*, is widened to 115.4 (2)°. Conversely, both angles between the thf and water contacts are reduced to 101.6 (2) and 107.5 (2)°. The tetraphenylborate anion, in which the centres B1, C21, C24, C31 and C34 are located in the mirror plane, exhibits the expected distances and bond angles.

Li$^+$ cations are frequently tetracoordinated with tetrahedral geometry, but slight deviations from an ideal tetrahedron are common. The average O—Li—O angle of eleven Li(thf)$_4$ complexes registered in the Cambridge Structural Database (version 5.08) (Allen & Kennard, 1993) is 109.5 (39)°, but the values range from 103° to 122°. On comparison with these tetrakis(tetrahydrofuran)lithium complexes, the title compound with two of the thf ligands substituted by water molecules in the coordination sphere, deviates most strongly from tetrahedral geometry.

The interaction of Li$^+$ cations with donor ligands is largely of ion-dipole character and, therefore, the coordination is dominated by steric and crystal packing effects (Setzer & von Schleyer, 1985). The angle

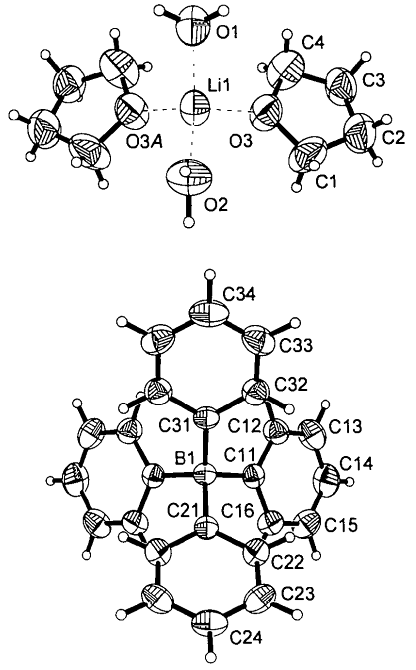


Fig. 1. Coordination sphere of the Li$^+$ cation showing lithium contacts as dotted lines and the non-coordinating tetraphenylborate anion.

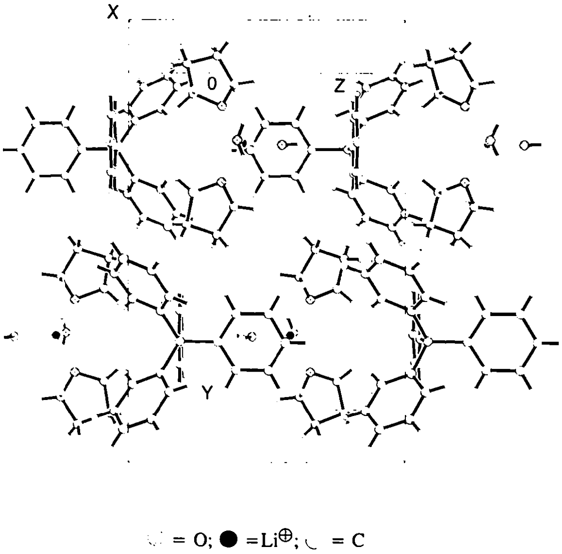


Fig. 2. Packing diagram along the *a* direction.

between the Li1—O3 vector and the normal to the C1—O3—C4 plane of tetrahydrofuran is 82.7 (2)°. This further supports the tendency of the Li^+ cation to adopt a position close to the plane of the ether grouping along the C—O—C bisector (Chakrabarti & Dunitz, 1982).

Experimental

Lithium tetraphenylborate was prepared from triphenylborane by adding phenyllithium in purified tetrahydrofuran (Wittig, Keicher, Rückert & Raff, 1949). Colourless blocks were crystallized from aqueous solution.

Crystal data

$[Li(C_4H_8O)_2(H_2O)_2]$-
$(C_{24}H_{20}B)$
$M_r = 506.39$
Orthorhombic
Pnma
$a = 17.252\,(3)$ Å
$b = 16.565\,(3)$ Å
$c = 10.422\,(2)$ Å
$V = 2978.4\,(9)$ Å^3
$Z = 4$
$D_x = 1.129$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 96 reflections
$\theta = 10$–$16.5°$
$\mu = 0.071$ mm^{-1}
$T = 200\,(1)$ K
Rectangular block
0.61 × 0.38 × 0.38 mm
Colourless

Data collection

Stoe Siemens AED-2 four-circle diffractometer
ω–θ scans
Absorption correction: none
3648 measured reflections
3555 independent reflections
2300 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0054$
$\theta_{\rm max} = 27.55°$
$h = -22 \rightarrow 22$
$k = -21 \rightarrow 8$
$l = 0 \rightarrow 13$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0495$
$wR(F^2) = 0.1607$
$S = 1.102$
3555 reflections
195 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.6761P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.275$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.306$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0029 (10)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Li1	0.4107 (3)	3/4	0.5996 (4)	0.0526 (10)
O1	0.30024 (13)	3/4	0.6178 (2)	0.0662 (6)
O2	0.4626 (2)	3/4	0.4372 (2)	0.0742 (7)
O3	0.43830 (10)	0.65270 (9)	0.68608 (14)	0.0716 (5)
C1	0.4871 (2)	0.5923 (2)	0.6376 (3)	0.1017 (10)
C2	0.4732 (2)	0.5186 (2)	0.7071 (3)	0.0916 (8)
C3	0.4351 (2)	0.54362 (14)	0.8290 (2)	0.0794 (7)
C4	0.4036 (2)	0.6255 (2)	0.8018 (2)	0.0861 (8)
B1	0.63098 (13)	3/4	0.1490 (2)	0.0327 (5)
C11	0.66935 (8)	0.67098 (9)	0.07685 (14)	0.0352 (3)
C12	0.73717 (9)	0.63262 (10)	0.1201 (2)	0.0454 (4)
C13	0.77121 (11)	0.56912 (12)	0.0542 (2)	0.0602 (5)
C14	0.73996 (12)	0.54118 (12)	−0.0586 (2)	0.0625 (5)
C15	0.67453 (11)	0.57816 (12)	−0.1061 (2)	0.0561 (5)
C16	0.64015 (9)	0.64175 (10)	−0.0393 (2)	0.0435 (4)
C21	0.53563 (12)	3/4	0.1355 (2)	0.0323 (4)
C22	0.49213 (9)	0.67886 (10)	0.1354 (2)	0.0400 (4)
C23	0.41129 (9)	0.67839 (11)	0.1343 (2)	0.0476 (4)
C24	0.37077 (13)	3/4	0.1331 (2)	0.0473 (6)
C31	0.64777 (12)	3/4	0.3047 (2)	0.0351 (5)
C32	0.65351 (10)	0.67900 (11)	0.3764 (2)	0.0447 (4)
C33	0.66730 (11)	0.67871 (13)	0.5085 (2)	0.0564 (5)
C34	0.6749 (2)	3/4	0.5742 (3)	0.0615 (8)

Table 2. *Selected geometric parameters (Å, °)*

Li1—O3$^{\rm i}$	1.907 (3)	O3—C4	1.420 (3)
Li1—O3	1.907 (3)	C1—C2	1.440 (4)
Li1—O2	1.914 (5)	C2—C3	1.490 (4)
Li1—O1	1.915 (5)	C3—C4	1.489 (3)
O3—C1	1.401 (3)		
O3$^{\rm i}$—Li1—O3	115.4 (2)	C1—O3—Li1	125.6 (2)
O3$^{\rm i}$—Li1—O2	107.5 (2)	C4—O3—Li1	124.4 (2)
O3—Li1—O2	107.5 (2)	O3—C1—C2	108.9 (2)
O3$^{\rm i}$—Li1—O1	101.6 (2)	C1—C2—C3	105.4 (2)
O3—Li1—O1	101.6 (2)	C4—C3—C2	104.6 (2)
O2—Li1—O1	123.6 (3)	O3—C4—C3	107.3 (2)
C1—O3—C4	109.5 (2)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

H centres of the water molecules were refined with free isotropic displacement parameters; all others were placed in geometrically idealized positions and refined with free isotopic displacement parameters using a riding model.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC XP* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93 *CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and complete geometry have been deposited with the IUCr (Reference: DU1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Holmium(III) 'Carbons Adjacent' Carborane Cluster, $[Li(C_6H_{16}N_2)_2][Li_2(C_6H_{16}N_2)_2\{HoCl_2(C_8H_{22}B_4Si_2)_2\}].0.5C_6H_6$

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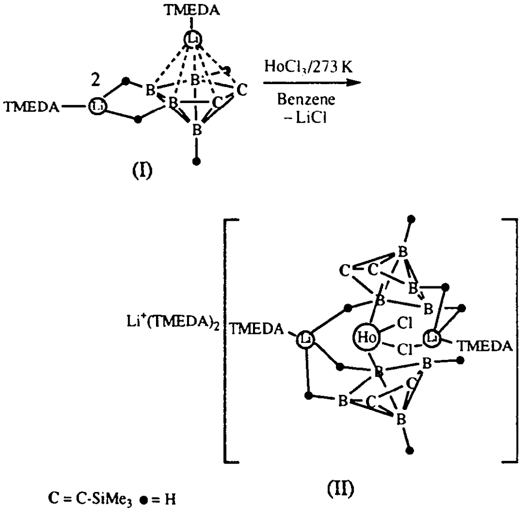
Abstract

The title compound, bis(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium μ-{1,1'-*commo*-1,1'-dichlorobis[2,3-bis(trimethylsilyl)-2,3-dicarba-1-holma-*closo*-heptaborato]}-$1\kappa^3H^{4',5',6}{:}2\kappa^2H^{4,5},2\kappa Cl$-bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium] benzene hemisolvate, $[Li(TMEDA)_2][\{1\text{-}Cl\text{-}1\text{-}(\mu\text{-}Cl)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,6\text{-}[(\mu\text{-}H)_2Li(TMEDA)]\text{-}4,4',5'\text{-}[(\mu\text{-}H)_3Li(TMEDA)]\}\text{-}1,1'\text{-}commo\text{-}Ho(2,3\text{-}C_2B_4H_4)_2].0.5C_6H_6$ (TMEDA = tetramethylethylenediamine), crystallized in a monoclinic space group, $P2_1/n$. The structure of this cluster consists of an Ho^{III} 'carbons adjacent' carborane bent-sandwich complex in which two Cl^- ions are present, in different bonding environments, in the primary coordination sphere of the Ho atom, giving a very distorted tetrahedral arrangement about the metal with the Ho—Cnt(1,2) = 2.378, 2.350 Å, Cnt(1)—Ho—Cnt(2) = 128.5°, Cnt(1)—Ho—Cl(1,2) = 107.9, 103.2°, Cnt(2)—Ho—Cl(1,2) = 110.6, 104.4°, and Cl(1)—Ho—Cl(2) = 97.17 (6)° (Cnt = C_2B_3 centroid). One of the *exo*-polyhedral Li(TMEDA) units is linked to both opposing C_2B_3 faces *via* three $B—H_{(terminal)}$ bonds and the other interacts with only one of the C_2B_3 faces *via* two $B—H_{(terminal)}$ groups with an additional linkage to the central Ho atom *via* an Ho—Cl—Li bridge.

Comment

It has been established that the reactivity of the dianionic $C_2B_4^-$ carborane ligands toward the lanthanide trihalides in anhydrous thf solvent results in the formation of unusual trinuclear lanthanacarborane clusters, in which an O atom triply bridges the three Ln atoms and a methoxy moiety binds to the apical Li atoms of the three *closo*-lithiacarboranes (Oki, Zhang & Hosmane, 1992; Zhang, Oki, Wang, Maguire & Hosmane, 1995; Hosmane *et al.*, 1994). Since all of the lanthanacarborane clusters are isostructural and their yields are reproduced even when the solvent, thf, was freshly distilled and extremely dehydrated, it is believed that a systematic reactivity pattern exists in this system. Nevertheless, it was speculated that the methoxide and O^{2-} ions might be the decomposition products of a side-reaction between the solvent and the reactant species. This speculation is not entirely inconceivable when one considers the high reactivity and great oxophilicity of the lanthanide compounds in general (Evans, 1985). In order to verify whether thf is the actual source for both the O^{2-} and the OMe^- units, we carried out a reaction between $HoCl_3$ and the TMEDA-solvated dilithiacarborane (I) (Hosmane, Saxena *et al.*, 1993) in a 1:2 ratio in an exclusively non-oxygen-containing solvent, benzene, at 273 K. We obtained the title compound, (II), as an air-sensitive orange crystalline solid in over 90% yield (Hosmane *et al.*, unpublished results).



The exclusive formation of (II) from (I) clearly indicates that the formation of the trinuclear Ho^{III} cluster is not possible in the absence of thf in the solvent mixture. Therefore, it is most likely that the thf is the

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