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# The composition and structure of lithium tetrakis(pentafluorophenyl) borate diethyletherate

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## ABSTRACT

Treatment of  $LiC_6F_5$  with  $B(C_6F_5)_3$  in equal volumes of light petroleum and diethyl ether at low temperature followed by slow warming to room temperature precipitates a microcrystalline solid which dries under vacuum to a material with the composition  $[Li(OEt_2)_3][B(C_6F_5)_4]$ . Crystallization from diethyl ether yields solvent dependent  $[Li(OEt_2)_4][B(C_6F_5)_4]$ , which has been crystallographically characterised.

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## 1. Introduction

The tetrakis(pentafluorophenyl)borate anion was first reported in 1963 [1]. The remarkable stability and low basicity of this anion has led to a huge number of applications as a weakly coordinating anion [2–4]. Its importance is reflected by the commercial availability of its salts. In particular a number of suppliers provide the lithium salt  $[\text{Li}(\text{Et}_2\text{O})_n][\text{B}(\text{C}_6\text{F}_5)_4]$ . However, there is considerable variation in the value of n, the number of associated ether molecules. The most frequently quoted composition is n = 2.5. It is obvious that the success of subsequent salt metathesis reactions, especially where the product is difficult to purify will be dependent upon anion purity and precise stoichiometry. We report here a procedure to isolate lithium tetrakis(pentafluorophenyl)borate diethyletherate in good yield with excellent anion purity. The composition of the isolated materials is compared to that of the crystalline salt, the solid state structure of which is reported herein.

## 2. Experimental

## 2.1. Material and methods

Syntheses were performed under anhydrous oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled over sodium-benzophenone (diethyl ether) or sodium (light petroleum, b.p. 40–60 °C). The NMR solvent (CD<sub>3</sub>CN) was dried over activated 4 Å molecular sieves and degassed by several freezethaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances (<sup>1</sup>H); <sup>19</sup>F is relative to CFCl<sub>3</sub>; <sup>11</sup>B is relative to  $F_3B$ ·OEt<sub>2</sub>. ( $C_6F_5$ )<sub>3</sub>B·OEt<sub>2</sub> was prepared according to the published procedure [5]. Elemental analyses were performed at the University of East Anglia. Additional reagents were purchased from Aldrich or Fluorochem and used without further purification.

## 2.2. Synthesis of $[Li(OEt_2)_3][B(C_6F_5)_4]$ (1)

A 1.65 M solution of *n*-butyl lithium in hexanes (14.5 mL) was added slowly to a solution of bromopentafluorobenzene (3 mL, 24.4 mmol) in a mixture of diethyl ether/light petroleum (200 mL/200 mL) at -78 °C and stirred for 1 h. Caution! LiC<sub>6</sub>F<sub>5</sub> is thermally unstable and may explode on warming; it must be prepared and maintained at -78 °C. This was followed by the dropwise addition of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B·OEt<sub>2</sub> (14.3 g, 24.4 mmol) dissolved in diethyl ether (300 mL). After 1 h at -78 °C the resulting suspension was warmed slowly to room temperature (ca. 20 °C/h). This gave a colourless microcrystalline solid, which was separated by filtration. The solid was dried under vacuum to give the desired salt as a white powder (16.35 g, 75%). The composition  $[Li(OEt_2)_3]$  $[B(C_6F_5)_4]$  was determined using the internal reference standard F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>. Anal. Calc. for C<sub>36</sub>H<sub>30</sub>BF<sub>20</sub>LiO<sub>3</sub>: C, 47.60; H, 3.33. Found: C, 46.79; H, 3.23%. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ 1.14 (t, 18H,  $J_{H-H}$  = 7 Hz,  $CH_3$  Et<sub>2</sub>O), 3.43 (q, 12H,  $J_{H-H}$  = 7 Hz,  $CH_2$  Et<sub>2</sub>O). <sup>11</sup>B NMR (96 MHz,  $CD_3$ CN):  $\delta$  –16.7. <sup>19</sup>F (282 MHz,  $CD_3$ CN):  $\delta$ -133.8 (m, 8F, o-F), -163.9 (td, 4F, J<sub>F-F</sub> = 20 and 7 Hz, p-F), -168.4 (m, 8F, *m*-*F*).



Note



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#### 2.3. Crystallographic analysis

Colourless blocks of  $[Li(OEt_2)_4][B(C_6F_5)_4]$  (**1a**) suitable for X-ray diffraction were obtained by cooling the solution obtained in 2.2. to -28 °C overnight.

## 2.3.1. Crystal data

C<sub>16</sub>H<sub>40</sub>O<sub>4</sub>Li, C<sub>24</sub>F<sub>20</sub>B, M = 982.5. Triclinic, space group PĪ (no. 2), a = 11.1432(2), b = 11.1625(2), c = 17.8069(4) Å, α = 78.734(2), β = 86.058(2), γ = 89.857(2)°, V = 2166.97(7) Å<sup>3</sup>. Z = 2, D<sub>c</sub> = 1.506 g cm<sup>-3</sup>, F(000) = 1000, T = 140(1) K, µ(Mo Kα) = 1.53 cm<sup>-1</sup>, λ(Mo Kα) = 0.71073 Å.

Crystals of [Li(OEt<sub>2</sub>)<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**1a**) were examined under perfluoropolyether oil, one, *ca* 0.56 × 0.44 × 0.21 mm, was mounted on a glass fibre and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo Kα radiation and graphite monochromator. Intensity data were measured by thin-slice  $\omega$ - and  $\varphi$ -scans. Total no. of reflections recorded, to  $\theta_{max}$  = 25.0°, was 39729 of which 7618 were unique ( $R_{int}$  = 0.038); 5670 were 'observed' with  $I > 2\sigma(I)$ .

Data were processed using the CRYSALIS-CCD and -RED [6] programs. The structure was determined by the direct methods routines in the SHELXS program [7a] and refined by full-matrix least-squares methods, on  $F^{2*}$ s, in SHELXL [7b]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their  $U_{1so}$  values were set to ride on the  $U_{eq}$  values of the parent carbon atoms. At the conclusion of the refinement,  $wR_2 = 0.102$  and  $R_1 = 0.070$  [7b] for all 7618 reflections weighted  $w = [\sigma^2(F_o^2) + (0.049P)^2 + 0.667P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ ; for the 'observed' data only,  $R_1 = 0.041$ .

In the final difference map, the highest peak (*ca* 0.59 e Å<sup>-3</sup>) was close to C71.

Scattering factors for neutral atoms were taken from reference [8]. Computer programs used in this analysis have been noted above, and were run through WINGX [9] on a Dell Precision 370 PC at the University of East Anglia.

Selected bond lengths and angles are given in Table 1.

## 3. Results and discussion

#### 3.1. Synthesis

Since its discovery, and because of its importance, there have been numerous revised syntheses of lithium tetrakis(pentafluorophenyl)borate [10]. We required a convenient laboratory route to a material with high anion purity and well defined stoichiometry. Song et al. reported that an ether-free salt could be obtained by treating  $B(C_6F_5)_3$  with  $C_6F_5Li$  in light petroleum [11]. However, in our hands this method yielded an off-white solid with several sets of <sup>19</sup>F resonances indicating poor purity. Marks has shown that related anions can be prepared cleanly using a solvent mixture of

Table I
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Selected bond lengths (Å) and angles (°) for $[Li(OEt_2)_4][B(C_6F_5)_4]$ (1a)
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B-C11	1.651(3)	C11-B-C41	114.46(17)
B-C41	1.653(3)	C11-B-C31	101.85(16)
B-C31	1.654(3)	C41-B-C31	113.49(17)
B-C21	1.658(3)	C11-B-C21	113.17(17)
		C41-B-C21	101.60(16)
		C31-B-C21	112.77(17)
Li-08	1.936(4)	08-Li-05	104.20(18)
Li-05	1.942(4)	08-Li-07	109.49(18)
Li-07	1.951(4)	05-Li-07	109.0(2)
Li-06	1.957(4)	08-Li-06	110.3(2)
		05-Li-06	116.90(19)
		07-Li-06	106.80(19)

$$C_{6}F_{5}Br + n-BuLi$$

$$Et_{2}O: Light Pet. (1:1)$$

$$F_{2}O: Light Pet. (1:1)$$

$$F_{2}O: Light Pet. (1:1)$$

$$-78^{\circ}C, R. T.$$

$$F_{3}OEt_{2} + C_{6}F_{5}Li \xrightarrow{-78^{\circ}C, R. T.}{75\%} [Li(OEt_{2})_{3}][B(C_{6}F_{5})_{4}]$$

$$1$$

Scheme 1. Preparation of 1.

diethyl ether and light petroleum [12]. When a  $B(C_6F_5)_3$  solution in diethyl ether was added at -78 °C to a solution of  $C_6F_5Li$  in a 1:1 mixture of diethyl ether and light petroleum and the reaction mixture allowed to warm up slowly to room temperature, a microcrystalline solid precipitated, which after drying corresponds to a 75% yield of [Li(OEt\_2)\_3][B(C\_6F\_5)\_4]. The <sup>19</sup>F NMR of the precipitate indicated very high (>98%) anion purity. Apparently any impurities and by-products remain in solution under these conditions (Scheme 1).

The number of associated diethyl ether molecules was determined by comparing results for integrating the <sup>1</sup>H and <sup>19</sup>F NMR spectra of **1** using *ca* 0.02 mL  $\alpha, \alpha, \alpha$ -trifluoro-*p*-xylene (F<sub>3</sub>CC<sub>6</sub>-H<sub>4</sub>CH<sub>3</sub>) as a reference (the spectra are given in the Supplementary Information). The number of diethyl ether molecules coordinated to the lithium cation (*n*) was found to be three, which is in good agreement with the results of the elemental analysis.

#### 3.2. Molecular structure

In order to better understand the composition of **1**, its solid state structure was determined. To the best of our knowledge, the solid state structure of a material with the formulation  $[\text{Li}(\text{Et}_2\text{O})_n][B(\text{C}_6\text{F}_5)_4]$  has not been reported. There are six crystal structures of lithium tetrakis(pentafluorophenyl)borate salts in the Cambridge Structural Database, but none with diethyl ether donors [13,14].

Crystallisation of **1**, from a saturated diethyl ether solution at -28 °C, yielded crystals which were very sensitive to solvent loss and required storage under the mother liquor.

The structure was determined to be  $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$  (**1a**) in which the asymmetric unit consists of an ion pair (Fig. 1). Both ions have a tetrahedral distribution of ligands around the central atoms; bond lengths and angles are reported in Table 1. There is nothing exceptional about the molecular structures of the cation and anion, which closely resemble those previously reported [14,15] and there is no close contact between the lithium centre and the anion.

Evidently, in diethyl ether solution, the lithium cation of lithium tetrakis(pentafluorophenyl)borate is fully solvated with four coordinated molecules of diethyl ether. This salt can be crystallized from diethyl ether solution. The facile loss of a solvent as volatile as diethyl ether leading to crystal degeneration is a common phenomenon but in this case it is not lattice solvent molecules but those donors associated with the cation that are lost. In our hands simple drying of the solid under vacuum at room temperature results in the loss of one molecule of diethyl ether per lithium centre giving  $[\text{Li}(\text{OEt}_2)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ . Presumably continued vacuum-drying perhaps at elevated temperatures might result in the slow loss of further molecules of diethyl ether.

Close inspection of the supramolecular architecture of **1a** (Fig. 2) reveals a lattice structure consisting of layers of the anion alternating with layers of the cation along the *b*-axis parallel to the (1 0 1) plane. These oppositely charged layers are attracted by coulombic interactions, there are no short charge-assisted C-H···F-C hydrogen bonds.



Fig. 1. Molecular structure of 1a. Thermal ellipsoids are shown at the 50% probability level. H-atoms on carbon have been omitted for clarity. One of the ethyl chains bound to O7 is disordered and both orientations were resolved and are represented.



**Fig. 2.** View along the *a*-axis of the layers of  $[B(C_6F_5)_4]^-$  and  $[Li(OEt_2)_4]^+$  in **1a**. Atoms appear by colour: B (pink), Li (purple), C (grey), O (red), F (green). Hydrogen atoms have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 4. Conclusion

A modification of the literature procedure yields the lithium tetrakis(pentafluorophenyl)borate diethyletherate salt in good yield and excellent purity and a consistent composition of  $[Li(OEt_2)_3][B(C_6F_5)_4]$ . When crystallised from diethyl ether solution the salt initially obtained is  $[Li(OEt_2)_4][B(C_6F_5)_4]$  which readily loses the first equivalent of ether. The solid state structure consists of layers of cations and anions.

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## Appendix A. Supplementary material

CCDC 743194 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2009.09.013.

#### References

- [1] A.G. Massey, A.J. Park, F.G.A. Stone, Proc. Chem. Soc. (1963) 212.
- [2] W.E. Piers, T. Chivers, Chem. Soc. Rev. (1997) 27.
- [3] E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.
- [4] W.E. Piers, Adv. Organomet. Chem. 52 (2005) 1.
- 5] S.J. Lancaster, <http://www.syntheticpages.org/pages/215>.;
- J.L.W. Pohlmann, F.E. Brinckman, Z. Naturforsch., Teil B 20 (1965) 5.
- [6] Programs CRYSALIS-CCD and -RED, Oxford Diffraction Ltd., Abingdon, UK, 2008.
- [7] G.M. Sheldrick, SHELX-97 Programs for (a) Crystal Structure Determination (SHELXS) and (b) Refinement (SHELXL), Acta Crystallogr., Sect. A 64 (2008) 112.
- [8] International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, 1992, pp. 500, 219 and 193.
- [9] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
- [10] For an example see: T.E. Krafft, Int. Pat. Appl., WO 98/17670, 1998, Boulder Scientific Company.
- [11] F. Song, RD. Cannon, S.J. Lancaster, M. Bochmann, J. Mol. Catal. A: Chem. 218 (2004) 21.
- [12] E.Y.-X. Chen, M.V. Metz, L. Li, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 6287.
- [13] D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.
- [14] (a) I.A. Guzei, C.E. Radzewich, R.F. Jordan, Acta Crystalloger., Sect. C56 (2000) 279;

(b) S.I. Pascu, T. Jarrosson, C. Naumann, S. Otto, G. Kaiser, J.K.M. Sanders, New J. Chem. 29 (2005) 80;
(c) D. Huerlander, N. Kleigrewe, G. Kehr, G. Erker, R. Frohlich, Eur. J. Inorg.

Chem. (2002) 2633;

- (d) H. Shen, I.M. Steele, R.F. Jordan, Acta Crystallogr. Sect. C59 (2003) m405;
  (e) M. Bolte, I. Ruderfer, T. Muller, Acta Crystallogr., Sect. E61 (2005) m1581;
  (f) J.D. Masuda, D.W. Stephan, Can. J. Chem. 83 (2005) 477.
  [15] Y. Sun, M.V. Metz, C.L. Stern, T.J. Marks, Organometallics 19 (2000) 1625.