Short Communication

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Daniel Duvinage, Artem Schröder, Enno Lork and Jens Beckmann*

New crystal structures of alkali metal tetrakis(pentafluorophenyl)borates

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Abstract: The crystal structures of the salts $[\text{Li}(1,2\text{-F}_2\text{C}_6\text{H}_4)] [\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) and $\text{Cs}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) comprise six $\text{Li}\cdots\text{F}$ contacts (1.965(3) – 2.312(3) Å) and twelve $\text{Cs}\cdots\text{F}$ contacts (3.0312(1) – 3.7397(2) Å), respectively, which are significantly shorter than the sum of van der Waals radii (3.29 and 4.90 Å).

Keywords: lithium; caesium; boron; borate ion; weakly coordinating anion

Polyfluorinated tetraarylborate ions, such as $[\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]^-$ “BAR[−]” and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Scheme 1), have received numerous applications as weakly coordinating anions (Krosssing and Raabe, 2004; Riddlstone et al., 2018), which also stimulated research into their alkali metal salts. Very recently, for the former, the crystal structures of $[\text{Li}(\text{H}_2\text{O})][\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$, $\text{M}[\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$ ($\text{M} = \text{Na}, \text{K}$) were described (Martínez-Martínez and Weller, 2019). For the latter, the crystal structures of $[\text{Li}(\text{C}_6\text{H}_6)][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{benzene}$ (Bolte et al., 2005), $[\text{Li}(\text{MeC}_6\text{H}_5)][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{toluene}$, $[\text{Li}(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Li}(\text{Et}_2\text{O})_4][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{CH}_2\text{Cl}_2$ (Kuprat et al., 2010; Martin et al., 2010), $[\text{Li}(\text{MeCN})_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (Zhang et al., 2012) and $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ (Protchenko et al., 2016) were reported. In this work we convey two new crystal structures of the same anion.

Crystals of $[\text{Li}(1,2\text{-F}_2\text{C}_6\text{H}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) were obtained by recrystallization of $[\text{Li}(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$ from 1,2-difluorobenzene. The key feature of **1** (Figure 1) is the presence of six $\text{Li}\cdots\text{F}$ contacts (1.965(3) – 2.312(3) Å) that are significantly shorter than the sum of van der Waals radii (3.29 Å) and the absence of π -interactions between cation

the electron poor aromatic rings. By contrast, in the crystal structure of $[\text{Li}(\text{C}_6\text{H}_6)][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{benzene}$ (Bolte et al., 2005) and $[\text{Li}(\text{MeC}_6\text{H}_5)][\text{B}(\text{C}_6\text{F}_5)_4]\cdot\text{toluene}$ (Kuprat et al., 2010), the cations show also π -interactions with the electron rich solvate molecules. The cesium salt $\text{Cs}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) crystallized in the rare cubic space group $I\bar{4}3d$ ($a = 19.213(1)$ Å). It is isostructural with the previously known thallium compound $\text{Tl}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($a = 19.10(1)$ Å) (Parvez et al., 2005). The cell volume of **2** ($V = 7092(1)$ Å³) is smaller than that of $\text{Tl}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($V = 6962(8)$ Å³), which can be attributed to the smaller ion radius of cesium (1.67 Å) compared to thallium (1.5 Å). The key feature of **2** (Figure 2) is the presence of twelve $\text{Cs}\cdots\text{F}$ contacts (3.0312(1)–3.7397(2) Å), respectively, which are significantly shorter than the sum of van der Waals radii (4.90 Å). These distances are consistent with those observed for $\text{Cs}[\text{H}_2\text{NB}_2(\text{C}_6\text{F}_5)_6]$, which shows even sixteen $\text{Cs}\cdots\text{F}$ contacts (Pollak et al., 2016).

1 X-ray crystallography

Single crystals of **1** were obtained by drying $[\text{Li}(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$ in high vacuum ($5\cdot 10^{-3}$ bar) at 140°C for 24 h and recrystallization from 1,2-difluorobenzene and *n*-hexane (Romanato et al., 2010). Single crystals of **2** were obtained by ion exchange of **1** in 1,2-difluorobenzene with Cesium fluoride followed by filtration and addition of *n*-hexane (Mon et al., 2013). Intensity data were collected on a Bruker Venture D8 diffractometer with graphite-monochromated Mo-K α (0.7107 Å) radiation. The structure was solved by direct methods and difference Fourier synthesis with subsequent Full-matrix least-squares refinements on F^2 , using all data (Dolomanov, 2009). All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 1974618 (**1**) and 1974619 (**2**).

* **Corresponding author: Jens Beckmann**, Institut für Anorganische Chemie und Kristallographie, Universität Bremen, Leobener Straße 7, 28359 Bremen, Germany, e-mail: j.beckmann@uni-bremen.de
Daniel Duvinage, Artem Schröder and Enno Lork, Institut für Anorganische Chemie und Kristallographie, Universität Bremen, Leobener Straße 7, 28359 Bremen, Germany

Scheme 1: Weakly coordinating polyfluorinated tetraarylborate “BArF” ions.

Figure 1: Crystal structure of $[\text{Li}(1,2\text{-F}_2\text{C}_6\text{H}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ (1) showing 50% probability ellipsoid and the essential atomic numbering. Cation anion contacts [Å]: Li1-F1 2.053(3), Li1-F2 2.090(3), Li1-F11 1.968(3), Li1-F21 1.965(3), Li1-F44a 2.312(3), Li1-F45a 2.018(3).

Figure 2: Crystal structure of $\text{Cs}[\text{B}(\text{C}_6\text{F}_5)_4]$ (2) showing 50% probability ellipsoid and the essential atomic numbering. Cation anion contacts [Å]: Cs1-F1 3.0312(1), Cs1-F2 3.7397(2), Cs1-F3 3.1943(1), Cs1-F5 3.3292(1).

Table 1: Crystal data and structure refinement of $[\text{Li}(1,2\text{-F}_2\text{C}_6\text{H}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ (1) and $[\text{CsB}(\text{C}_6\text{F}_5)_4]$ (2).

	1	2
Formula	$\text{C}_{30}\text{H}_4\text{BF}_{22}\text{Li}$	$\text{C}_{24}\text{BCSF}_{20}$
Formula weight, g mol ⁻¹	800.08	394.74
Crystal system	monoclinic	cubic
Crystal size, mm	0.5 × 0.5 × 0.4	0.3 × 0.3 × 0.3
Space group	$P2_1/n$	$I\bar{4}3d$
<i>a</i> , Å	13.9256(5)	19.213(1)
<i>b</i> , Å	12.4375(5)	19.213(1)
<i>c</i> , Å	15.9947(5)	19.213(1)
α , °	90	90
β , °	92.016(1)	90
γ , °	90	90
<i>V</i> , Å ³	2768.6(2)	7092(1)
<i>Z</i>	4	12
ρ_{calcd} , Mg m ⁻³	1.920	2.281
<i>T</i> , K	100	100
<i>m</i> (Mo <i>K</i> α), mm ⁻¹	0.215	1.741
<i>F</i> (000)	1560	4608
θ range, deg	2.20 to 33.23	2.60 to 30.43
Index ranges	$-21 \leq h \leq 21$ $-18 \leq k \leq 19$ $-24 \leq l \leq 24$	$-27 \leq h \leq 23$ $-27 \leq k \leq 23$ $-20 \leq l \leq 27$
No. of reflns collected	108154	23264
Completeness to θ_{max}	99.9%	99.9%
No. indep. Reflns	10630	1805
No. obsd reflns with (<i>I</i> > 2σ(<i>I</i>))	8391	1695
No. refined params	487	105
Goof (<i>F</i> ²)	1.037	1.110
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2σ(<i>I</i>))	0.0444	0.0277
<i>wR</i> ₂ (<i>F</i> ²) (all data)	0.1272	0.0749
(Δ/ σ) _{max}	< 0.001	< 0.001
Largest diff peak/hole, e Å ⁻³	0.706 / -0.505	0.514 / -0.632

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Conflict of interest: One of the authors (Jens Beckmann) is a member of the Editorial Board of Main Group Metal Chemistry.

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