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Organotrifluoroborates as attractive self-assembling systems: the case of bifunctional dipotassium phenylene-1,4-bis(trifluoroborate)[†]

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The first structure of an aromatic bis(trifluoroborate) dipotassium salt, elucidated by the combination of crystallography, DFT calculations, topological and non-covalent interaction analysis, discloses a 3D network undergoing spontaneous self-assembly thanks to the massive participation of weak intra- and inter-molecular interactions for which fluorine atoms proved to play a leading role.

In recent years, growing attention has been paid to the chemistry of organoboron compounds as useful and valuable reagents for many transition-metal-catalysed¹ and also “metal-free”² C–C bond-forming reactions. Organotrifluoroborate salts, in particular, have been shown to be attractive and versatile boronic acid surrogates.³ This is either because of their exceptional stability toward oxygen and common reagents or because of their higher nucleophilicity and excellent functional group tolerance. Thus, it is no surprise that the recent burst in activity in their chemistry has seen them more and more as leading actors in a variety of chemical scenarios ranging from palladium-catalysed cross-coupling reactions³ and stereoselective rhodium-catalysed 1,2- and 1,4-addition reactions⁴ for the construction of complex organic frameworks.⁵

However, despite the exponential growth of papers dedicated to potassium organotrifluoroborates in the last 10 years, few investigators have, to date, concentrated their research on the structures of such salts.⁶ The few X-ray structure determinations reported so far for compounds containing a benzene

ring carrying at least one –BF₃K group⁷ reveal the singular and unique feature of each organotrifluoroborate salt in which large polarizable cations such as K⁺ (which are significantly better charge-delocalizing than Li⁺) permit extended crystal lattices to form because of their multihapto coordinations.⁸ Such molecular structures are often held together by weaker coordinations (*e.g.*, C–H⋯π, K⋯π and π–π interactions) and, sometimes, also by long-range electrostatic forces. All these interactions contribute to define the final architecture of the packing.

This self-assembly aspect of organotrifluoroborates is surely amazing and worth investigating because the peculiar nature of each salt may promote self-organization and thus the obtainment of functional supramolecular architectures with potential interest in many fields (*e.g.*, materials science, catalysis, sensing and separations) as has recently been ascertained in the case of boronic acids, which have been shown to undergo spontaneous supramolecular assembly either with themselves or with other *N*-donor compounds.⁹ Aromatic and heteroaromatic bis- and poly(trifluoroborate) compounds have also been successfully employed in the manufacture of novel conjugated polymers with excellent and interesting electron-transport properties.¹⁰ Thus, the design and synthesis of novel polyfunctional aromatic compounds carrying more than one trifluoroborate group onto the aromatic core is fascinating and challenging both from a crystallographic and a synthetic perspective in order to chemoselectively replace them in multistep organic synthesis and to obtain new functional structural motifs.

Recently, we have described the preparation of bifunctional dipotassium phenylene-1,4-bis(trifluoroborate) **2** from the corresponding commercially available bis(boronic acid) **1** (Scheme 1) and its successful employment in one-pot double

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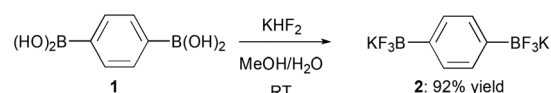
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Scheme 1 Synthesis of bis(trifluoroborate) **2** from bis(boronic acid) **1**.



Suzuki–Miyaura coupling reactions for the obtainment of conjugated tri(hetero)aryl derivatives.¹¹

In this paper, we present the first structural investigations on such a salt (**2**) which provide detailed insight on the presence of an impressive multitude of weak inter- and intra-molecular interactions responsible for its self-assembly into a new 3D network.

Bis-trifluoroborate **2**, directly obtained as a white free-flowing powder in 92% yield, has been crystallized at room temperature by slow evaporation from a solution of 2 : 1 acetone/H₂O (in ratio 2 : 1) and colourless needles (mp 342 °C) have been collected. Bis(trifluoroborate) **2**, crystallizes in a tetragonal crystal system, in the space group *I*₄*/acd* with the cell parameters *a* = 17.597(9) Å and *c* = 40.203(9) Å. The asymmetric unit consists of 1.5 independent molecules of C₆H₄B₂F₆, 5 K atoms (one of them at the general position, and the rest at special positions with a site occupancy factor of 0.5) and half a molecule of H₂O. A view of the refined crystal structure is shown in Fig. 1 where short K $\cdots$ F and K $\cdots$ O contacts are distinguishable. Of note, the H atom of the 0.5 H₂O molecule points towards the benzene ring, the distance between the centroid of the aromatic ring and the H atom (labelled as H100) being 2.475 Å, thereby suggesting the presence of an aromatic OH $\cdots$ π interaction (*vide infra*).¹²

The C–C bond lengths of the aromatic ring vary from 1.383 (4) Å up to 1.397(4) Å and are thus consistent with π delocalization; the ring is, indeed, essentially planar. The B–F bond lengths range from 1.391(4) Å for B3–F9 to 1.447(3) Å for B1–F2 (Table S1, ESI†) and are in agreement with the values reported in the literature.^{7c,f} All the three F atoms belonging to BF₃ groups lie out of the plane of the aromatic ring. Analogous to what has been reported for other organotrifluoroborates,^{7f,10b,c} the coordination geometry around all K⁺ cations is irregular and cannot be conveniently described by any polyhedron,¹³ K $\cdots$ F contacts ranging from 2.621(2) Å (K4 $\cdots$ F8) to

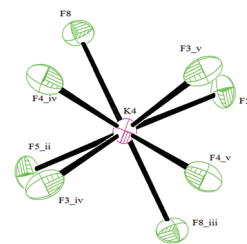


Fig. 2 The environment of K4 cation. Symmetry codes: (i) $-x + 1, -y + \frac{1}{2}, z$; (ii) $-x + 1, -y, -z$; (iii) $x, y + \frac{1}{2}, -z$; (iv) $-y + \frac{3}{4}, x - \frac{1}{4}, -z + \frac{1}{4}$; (v) $y + \frac{1}{4}, -x + \frac{3}{4}, -z + \frac{1}{4}$.

3.382(3) Å (K3 $\cdots$ F9). In particular, cations K1, K2 and K3 all have ten short contacts to F atoms (most of them less than 3.0 Å, see the ESI†), and two slightly longer contacts to B atoms (Table S1, ESI†). The environment of the K4 cation, which is depicted in Fig. 2, shows eight short contacts to F atoms in the range 2.621(2) Å–3.041(2) Å. In the case of a K5 cation, four interactions with F atoms less than 3.0 Å, one to oxygen 2.7247(17) Å and two distances to carbons C5 and C8 longer than 3.3 Å are present, instead.

Fig. 3 depicts the packing of the title compound revealing the presence of K cation layers bridged by C₆H₄B₂F₆ and H₂O molecules *via* K $\cdots$ F, K $\cdots$ O, OH $\cdots$ π and K $\cdots$ aryl interactions. Thus, despite its apparent structural and spectroscopic simplicity,[¶] the overall 3D network of the salt **2** is made up of C₆H₄ layers coated with BF₃ groups either side. The fluorinated walls leave enough space to coordinate the potassium cations of which one is slightly pulled towards the ring centre by the water molecule.

The study of non-covalent interactions, and in particular of the contribution of organic fluorine in the formation of different supramolecular motifs, is an expanding area of research amongst the scientific community and has recently gained much interest both in crystal engineering for the systematic design of advanced functional materials^{14,15} and in asymmetric synthesis.¹⁶ Thus, to gain further insights, the interactions within the crystal were investigated in detail by the use of an NCI (non-covalent interaction) analysis,¹⁷ which is an informative and illustrative tool to display hydrogen

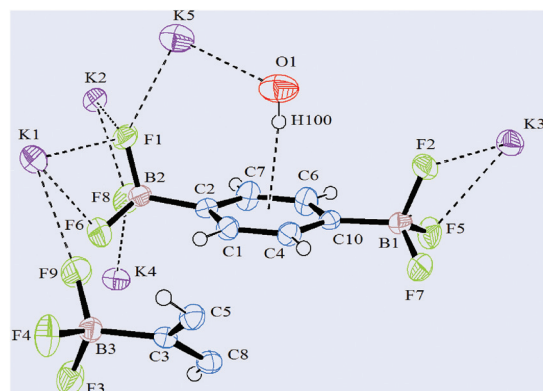


Fig. 1 ORTEP-plot of the asymmetric unit of the title compound **2** with ellipsoids plotted at the 50% probability level. Short K $\cdots$ F, K $\cdots$ O contacts and OH $\cdots$ π interactions are drawn as dashed lines. Colour codes in the electronic version of the paper: carbon (blue), boron (light brown), fluorine (green), potassium (violet) and oxygen (red). Hydrogen atoms are also drawn as small spheres.

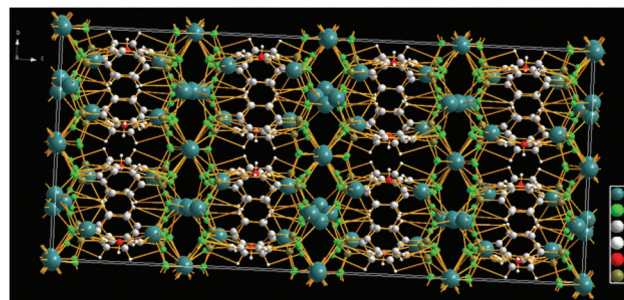


Fig. 3 3D packing of the title compound **2**.



bonds and weak inter- and intramolecular interactions based on the calculated electron density. In addition, we have adopted Bader's atoms in molecules (AIM) concept for identifying a bond path and a bond critical point (BCP) from the electron density.¹⁸ In Fig. 4, the water $\text{OH}\cdots\pi$ interaction (*vide supra*) is clearly identified and visualized as an interaction surface. The hydrogen bond critical point is visualized as a light blue sphere and the hydrogen bond path is seen as a dotted line. The hydrogen bond strength was quantified to be *ca.* -8 kcal mol^{-1} by DFT calculations.¹⁹ It is also found that H_2O interacts with the potassium cation K5, quantified to *ca.* -7 kcal mol^{-1} . In addition, the two aromatic rings are stabilized by side-on dispersive $\text{CH}\cdots\pi$ interactions as visualized by the interaction surface and the two BCP spheres and bond paths. Interestingly, the fluorines in the BF_3 group are observed to feature three distinctly different interactions (Fig. 4): $\text{F}\cdots\text{F}$ halogen bond interaction,¹⁵ $\text{CH}\cdots\text{F}$ interaction to an aromatic hydrogen, and in addition also to the potassium cation. A more detailed characterization of these interactions is found in Fig. S1 in the ESI.† The short distances between $\text{K}\cdots\text{C}$ were, by the BCP and bond path analysis, actually found to be due to agostic interactions²⁰ between potassium and the aromatic CH hydrogens rather than due to the carbons. This conclusion was supported by an NBO-analysis, which showed

electron delocalisation from the two aromatic C–H bonds to the potassium cations (for further details, see Fig. S2, ESI†). Thus, by the use of the NCI and BCP analysis we have been able to demonstrate the presence of $\text{K}\cdots\text{F}$, $\text{K}\cdots\text{O}$, $\text{K}\cdots\text{HC}$, $\text{OH}\cdots\pi$, $\text{CH}\cdots\pi$, $\text{F}\cdots\text{F}$ and $\text{CH}\cdots\text{F}$ inter- and intramolecular interactions. It is thus manifested that the fluorines in the tri-fluoroborate group are of great importance for stabilization and formation of the crystal structure of compound 2.

Conclusions

In summary, single-crystal X-ray diffraction analysis of a structure containing a benzene ring with two $-\text{BF}_3$ groups reveals an unprecedented 3D supramolecular network assembled by $\text{K}\cdots\text{F}$, $\text{K}\cdots\text{O}$, $\text{OH}\cdots\pi$ and $\text{K}\cdots\text{aryl}$ interactions. A large contribution to the stability of the packing, however, is offered by additional non-conventional weak inter- and intramolecular interactions (*e.g.*, $\text{K}\cdots\text{HC}$, $\text{CH}\cdots\pi$, $\text{F}\cdots\text{F}$ and $\text{CH}\cdots\text{F}$), as unveiled by the BCP and bond path analysis. It is worth mentioning that the participation of organic fluorine in the formation of intermolecular interactions has always been a matter of concern.¹⁵

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Notes and references

§ Torsion angles $\text{C4-C10-B1-F2} = -88.59^\circ$, $\text{C4-C10-B1-F5} = 153.67^\circ$, $\text{C4-C10-B1-F7} = 30.19^\circ$, $\text{C1-C2-B2-F1} = 86.21^\circ$, $\text{C1-C2-B2-F8} = -156.72^\circ$, $\text{C1-C2-B2-F6} = -33.34^\circ$, $\text{C8-C3-B3-F9} = -89.42^\circ$, $\text{C8-C3-B3-F4} = 150.34^\circ$, and $\text{C8-C3-B3-F3} = 32.36^\circ$.

¶ The solution structure of 2 exhibits a single set of signals: $^1\text{H-NMR}$ (400 MHz, DMSO-d_6): $\delta = 7.04$ (s, 4H); $^{13}\text{C-NMR}$ (150 MHz, DMSO-d_6): $\delta = 145.4$ (br s); $^{19}\text{F-NMR}$ (376 MHz, DMSO-d_6): $\delta = -137.5$ (br s); $^{11}\text{B-NMR}$ (192 MHz, DMSO-d_6): $\delta = 4.38$ (br s).

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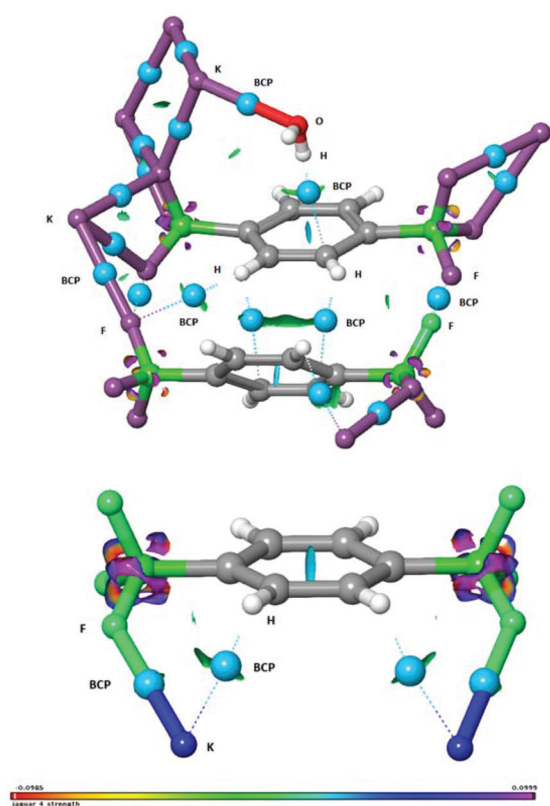


Fig. 4 Non-covalent interaction (NCI) analysis of extracts of the crystal structure of compound 2. BCP = bond critical point marked with light-blue spheres and bond paths with dotted lines.



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