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

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Structural Characterization of the title compound 2

X-ray diffraction experiments were carried out at two different temperature: 298 K and 100 K. Data were collected either on a Bruker-Nonius KappaCCD single crystal diffractometer equipped with a charge-coupled device (CCD detector) at 298 K or on a Bruker TXS diffractometer equipped with a rotating anode with mirror-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 100 K. A colourless needle-shaped single crystal of the title compound **2** (dimensions 0.10 × 0.15 × 0.35 mm) has been selected and mounted on a glass fiber for the X-ray diffraction measurements. The automatic data collection was performed by the *COLLECT*[1a] software, cell determination and refinement by *DIRAX*[1b] and data reduction by *EVAL*[1a]. Absorption effects were corrected by *SADABS*[1c] *via* a semi-empirical approach. The crystal structure was solved by SIR2011, the updated version of the package SIR2008[1d] and refined by SHELXL-2013.[1e] Additional software: *WinGX*,[1f] for preparing the material for publication, ORTEP-3[2] for molecular graphics. All the non-H atoms have been located by SIR2011 and anisotropically refined by SHELXL-2013. H atoms have been placed at calculated positions and refined according to a riding model approximation except for the H atom of the 0.5 H_2O molecule. It has been located by difference Fourier synthesis and it has been freely refined. Final values of agreement factors are R = 4.14% and wR = 9.03% in case of $F_o^2 > 2\ \sigma(F_o^2)$; the number of refined parameters and the number of reflections actively used are 228 and 2365, respectively (see Table S2 for additional crystallographic information).

Table S1. Selected bond lengths (Å) (°) for the title compound **2**.

K1	-	F6	2.757(2)	K3	-	F6^{v}	2.882(2)
K1	-	F6^{i}	2.757(2)	K3	-	F6^{ix}	2.882(2)
K1	-	F7^{ii}	2.767(2)	K3	-	F9^{v}	3.382(3)
K1	-	F7^{iii}	2.767(2)	K3	-	F9^{ix}	3.382(3)
K1	-	F9^{i}	2.845(2)	K3	-	B1^{viii}	3.407(3)
K1	-	F9	2.845(2)	K3	-	B1	3.407(3)
K1	-	F1	2.868(2)	K4	-	F8^{x}	2.621(2)
K1	-	F1^{i}	2.868(2)	K4	-	F8	2.621(2)
K1	-	F2^{iii}	2.8917(19)	K4	-	F5^{v}	2.678(2)
K1	-	F2^{ii}	2.8917(19)	K4	-	F5^{xi}	2.678(2)
K1	-	B2^{i}	3.422(4)	K4	-	F4^{vii}	2.9494(19)
K1	-	B2	3.422(4)	K4	-	F4^{xii}	2.9495(19)
K2	-	F7^{iv}	2.6790(19)	K4	-	F3^{vii}	3.041(2)
K2	-	F7^{v}	2.6791(19)	K4	-	F3^{xii}	3.041(2)
K2	-	F8	2.703(2)	K5	-	F1	2.633(2)
K2	-	F8^{i}	2.703(2)	K5	-	F3^{xiii}	2.643(2)
K2	-	F4^{vi}	2.846(2)	K5	-	F2^{ii}	2.659(2)
K2	-	F4^{vii}	2.846(2)	K5	-	F4^{vi}	2.678(2)
K2	-	F1	2.980(2)	K5	-	O1	2.7247(17)
K2	-	F1^{i}	2.980(2)	K5	-	C5^{vi}	3.369(3)
K2	-	F9^{vii}	3.151(3)	K5	-	C8^{xiii}	3.496(3)
K2	-	F9^{vi}	3.151(3)	B1	-	F2	1.447(3)
K2	-	B2	3.471(3)	B1	-	F5	1.415(4)
K2	-	B2^{i}	3.471(3)	B1	-	F7	1.408(4)
K3	-	F2^{viii}	2.7557(17)	B2	-	F1	1.440(3)
K3	-	F2	2.7558(17)	B2	-	F6	1.411(4)
K3	-	F3^{v}	2.787(2)	B2	-	F8	1.413(4)
K3	-	F3^{ix}	2.787(2)	B3	-	F3	1.426(4)
K3	-	F5	2.7931(19)	B3	-	F4	1.424(3)
K3	-	F5^{viii}	2.7931(19)	B3	-	F9	1.391(4)

Symmetry codes: (*i*) *–x+½ , y, –z*; (*ii*) *-y+¼, –x+¼, –z+¼*, (*iii*) *y+¼, –x+¼, z–¼*; (*iv*) *–y+¼, -x+¾, z–¼*; (*v*) *y+¼, –x+¾ ,–z+¼* ; (*vi*) *-x+½, y+ ½ , z*; *(vii) x, y+ ½ ,–z; (viii) –x+½, –y+½, –z+½; (ix) –y+ ¼, x –¼, z+¼*; *(x) –x+*1*, -y+½, z*; (*xi*) *-y+¾, x–¼, –z+¼*; (*xii*) *–x+*1, *–y, –z*; (*xiii*) *x-½, , –y, z.*

Table S2. Fractional atomic coordinates (Å), crystallographic occupancy factor and equivalent isotropic thermal factors U_{iso} (Å^2) for the title compound **2**.

Atom	x	y	z	Occ	U_{iso}
K1	0.2500	-0.0097	0.000	0.500	0.0365
K2	0.2500	0.2810	0.000	0.500	0.0342
K3	0.2500	0.2500	0.2500	0.500	0.0410
K4	0.5000	0.2500	0.0185	0.500	0.0390
K5	0.1188	0.1380	0.0631	1.000	0.0476
F1	0.2540	0.1320	0.0352	1.000	0.0427
F2	0.2566	0.1300	0.2060	1.000	0.0380
F3	0.4814	-0.1332	0.0366	1.000	0.0484
F4	0.3898	-0.2237	0.0355	1.000	0.0470
F5	0.3670	0.1955	0.2095	1.000	0.04420
F6	0.3675	0.0724	0.0277	1.000	0.0487
F7	0.3680	0.0659	0.2093	1.000	0.04570
F8	0.3618	0.2008	0.0299	1.000	0.04570
F9	0.3571	-0.1002	0.0352	1.000	0.05860
C10	0.3399	0.1311	0.1550	1.000	0.02480
C2	0.3406	0.1322	0.0840	1.000	0.02480
C3	0.4065	-0.1533	0.0892	1.000	0.02410
C4	0.3408	0.0639	0.1365	1.000	0.02830
H4	0.3408	0.0175	0.1477	1.000	0.03400
C5	0.3574	-0.2006	0.1070	1.000	0.02760
H5	0.3245	-0.2321	0.0953	1.000	0.03300
C1	0.3416	0.0646	0.1020	1.000	0.02790
H1	0.3429	0.0186	0.0905	1.000	0.03300
C6	0.3404	0.1981	0.1370	1.000	0.03520
H6	0.3404	0.2441	0.1484	1.000	0.0420
C7	0.3408	0.1990	0.1024	1.000	0.03610
H7	0.3413	0.2454	0.0914	1.000	0.04300
C8	0.4523	-0.1060	0.1085	1.000	0.02630
H8	0.4852	-0.0723	0.0979	1.000	0.03200
O1	0.1600	0.0900	0.1250	0.500	0.05540
H100	0.2050	0.0970	0.1256	1.000	0.06700
B3	0.4080	-0.1515	0.0493	1.000	0.02790
B1	0.3346	0.1304	0.1946	1.000	0.02990
B2	0.3330	0.1338	0.0446	1.000	0.02920

Table S3. Crystallographic data for the title compound **2**.

Diffractometer	Bruker-Nonius KappaCCD diffractometer
Wavelength (Å)	$\lambda = 0.71073$, MoK_α
Colour, habit	Colourless, needle
Size/mm	$0.35 \times 0.15 \times 0.10$
Empirical formula	$(C_6H_4B_2F_6K_2)_3.H_2O$
Chemical formula weight	887.75
Crystal system	Tetragonal
Space group	$I4_1/acd$
a/ Å	17.597(9)
c/ Å	40.203(9)
V/Å^3	12449(9)
Z	32
μ/mm^{-1}	0.966
T/K	100 or 298[‡]
θ_{min} / θ_{max}	5.01/27.51
Completeness	0.993
Reflections: total/independent	72460 / 3565
R_{int}	8.8%
Number of reflections with $F_o^2 > 2\,\sigma(F_o^2)$	2365
Number of parameters	228
Final $R1$, $wR2$	4.14%, 9.03%
Highest peak, Deepest hole /e Å^{-3}	0.558, –0.618
Density/g cm^{-3}	1.895

[‡] No substantial differences in terms of bond lengths and bond angles were detected by measuring crystal parameters at the two indicated temperatures.

Computational details

Model systems for the computational studies were created from the crystal structure of **2**. Single-point energy calculations to quantify interaction energies were done using M06/LACVP+(d,p)[3] as implemented in Jaguar 8.4.[4] Non-covalent interaction analysis[5] and bond path analysis[6] were performed employing the implementations within Jaguar. The bond path analysis determines the topology of the calculated electron density and categorizes critical points. A (3,-1) bond critical point (BCP) indicates accumulation of electron density and hence a bond, and the line of maximum charge density between the bonded atoms determines the bond path.[6]

Structural analysis

In the crystal structure of compound **2**, the two aromatic rings are found to be stabilised by side-on dispersive CH···π interactions as visualized by the interaction surface, the two BCP spheres and bond paths (Fig. 4). The distances between the π-system and CH hydrogens are shown in Fig. S1. As can be seen, the CH···π distances are approximately 3.0 Å to the edge, and the distance to the aromatic ring centre is 3.3–3.5 Å, which are in the typical range for these type of interactions.[7] The detected halogen bond between the fluorines is found to be rather weak (3.1 Å), and the overall molecular constraints due to other interactions does not allow the B–F–F angle to become larger than 123–142° which is in between the classical type I (angle ~180°) and type II (angle ~90°) halogen bonds discussed in the literature.[8] Water interaction with an aromatic ring is a phenomena well discussed in the literature.[9] Here, we find the OH···π distance to be 2.5 Å (the O···π distance is 3.3 Å), which indicates a rather strong bond (ca. –8 kcal mol^{-1}). This is an effect of the water-potassium coordination, making the O–H bond more polarized and with more positive charge on the hydrogen than in a non-coordinated water molecule.

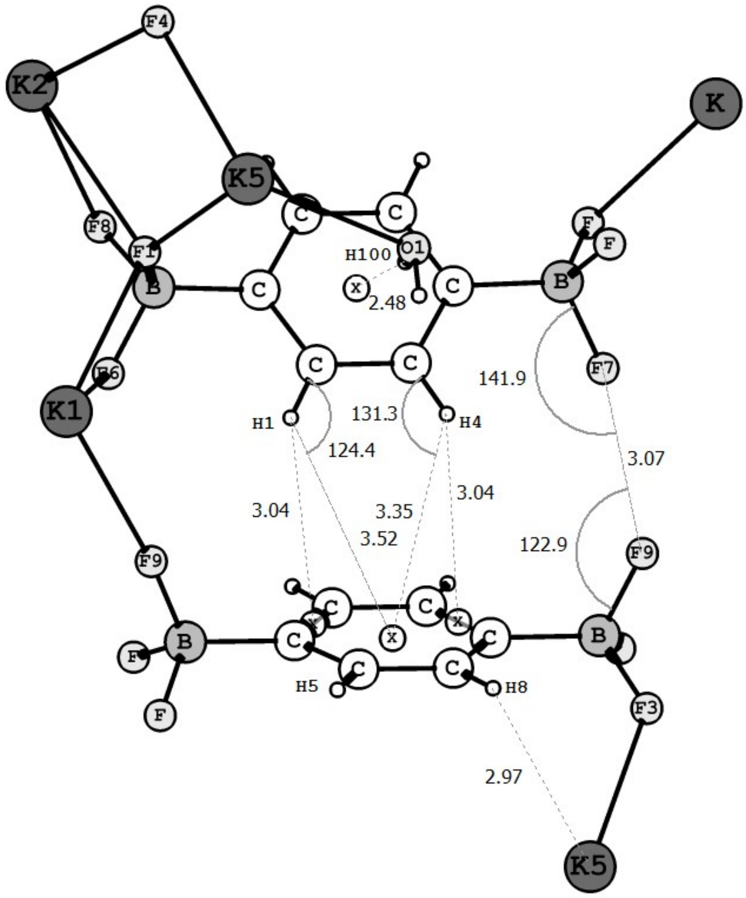

Fig. S1 Distances (in Å) and angles (in degrees) in the crystal structure of compound **2**. Atom type X denotes a dummy atom to indicate a specific position.

To characterize the interactions between the aromatic hydrogens and potassium we have been using NBO-analysis.[10a] From the analysis it is observed that electron delocalisation from the two aromatic C–H bonds to the potassium cations occur, indicating agostic interactions.[11] The perturbation interaction analysis within NBO estimates this to 0.45 kcal mol^{-1} for the K···H8C interaction, and 0.33 kcal mol^{-1} for the K···H5C interaction.[10b] The distances between the potassium cations and the aromatic CH hydrogens, forming agostic interactions, are displayed in Fig. S2, together with the corresponding K–C distances and C–H–K angles. The BCPs and bond paths for these interactions are seen in Fig. 4. The presence of K···HC interactions have been discussed before in the literature.[11a]

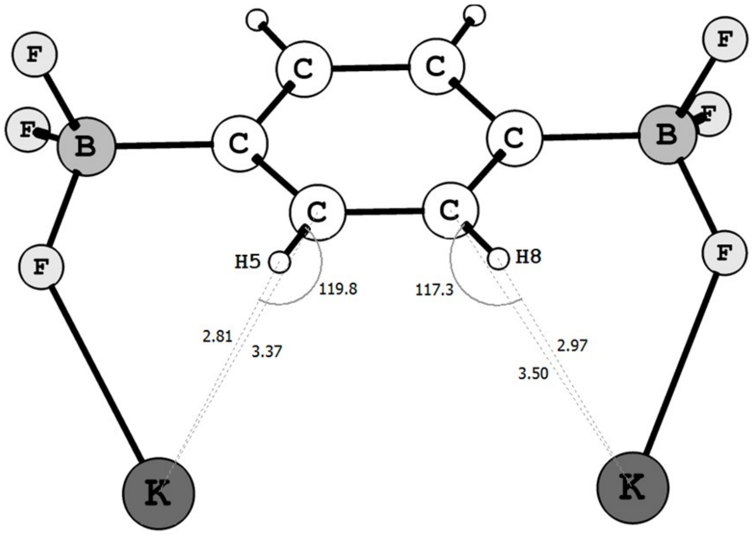

Fig. S2 Distances (in Å) and angles (in degrees) observed in the crystal structure of compound **2**.

In Table S4, we report on the characteristics of the different BCPs where we have used the fact that a negative sign of the second eigenvalue (λ_2) of the Laplacian ($\Delta^2\rho$) indicates an attractive stabilizing interaction.[5] This is multiplied by the electron density (ρ), which is related to the interaction strength.

Table S4. Non-covalent bond interaction analysis of compound **2**.

Bond critical path (BCP)	Sign(λ_2)*ρ (a.u.)
H100-π	-0.0099
K5-O1	-0.0173
H1-π	-0.0044
H4-π	-0.0047
F7-F9	-0.0042
F6-F9	-0.0050
H1-F9	-0.0022
K1-F9	-0.0101
K1-F6	-0.0135
K2-F1	-0.0807
K2-F4	-0.0122
K2-F8	-0.0154
K5-F1	-0.0174
K5-F4	-0.0175
K5-H5	-0.0060
K5-H8	-0.0045

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