

and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium Trifluorophenylborate

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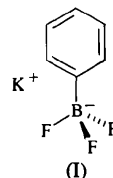
Abstract

X-ray structural analysis confirms that the title compound, potassium trifluorophenylborate, K⁺.C₆H₅BF₃⁻, contains the first structurally characterized example of a trifluorophenylborate anion. The C—C bond lengths of the phenyl ring lie within the range 1.38 (2)–1.41 (2) Å, consistent with π-electron delocalization; the three B—F bond lengths are 1.41 (1), 1.41 (1) and 1.43 (1) Å. The

anion can be considered as a Lewis acid complex of BF₃ and Ph⁻, and as expected from a simple VSEPR model, the geometry around the B atom is tetrahedral, although the presence of two different substituents around the B atom results in two distinct sets of bond angles, with significantly smaller values for the three F—B—F angles [104.4 (7), 106.0 (7) and 106.7 (9)°] compared with the remaining three C(phenyl)—B—F angles [112.1 (7), 112.9 and 114.1 (7)°].

Comment

This work is part of a general investigation into the structures of Lewis acids and their complexes, as an aid to efficient parameterization of Lewis acid complexes for molecular modelling (Allinger, 1977; Eliel, Allinger, Angyal & Morrison, 1965; Burkert & Allinger, 1982). The tetrafluoroborate and tetraphenylborate anions are widely used as counterions in both organic and inorganic chemistry, and the number of reports of crystal structures containing such anions run into the thousands. The crystal structure determination of the title compound, (I), is the first of an intermediate between these two anions, and thus, the effect of substitution of one of the F atoms by a phenyl group on the molecular geometry of the anion can be assessed. This asymmetric anion may also prove to be a better counter-ion than the tetrafluoroborate anion, which is frequently prone to crystallographic disorder.



X-ray structural analysis shows that potassium trifluorophenylborate consists of discrete K⁺ cations and BF₃Ph⁻ anions. The structure crystallizes in the non-centrosymmetric orthorhombic space group *Pca*2₁ with one independent molecule in the asymmetric unit. A perspective *ORTEPII* (Johnson, 1976) drawing of the trifluorophenylborate anion in the asymmetric unit is shown in Fig. 1.

The phenyl ring bond distances in the trifluorophenylborate anions are consistent with π-electron delocalization and lie within the range 1.38 (2)–1.41 (2) Å; similarly, the C—C—C bond angles are consistent with *sp*² hybridization and lie within the range 117.7(8)–121(1)°. The phenyl ring is essentially planar with only slight deviations from planarity (maximum deviation 0.01 Å).

The three B—F bond distances of 1.41 (1), 1.41 (1) and 1.43 (1) Å are within the range observed for compounds containing the related tetrafluoroborate anion. Recent literature examples include the selenium compound [(C₁₀H₁₂S₂Se₂)₂][BF₄], which has a

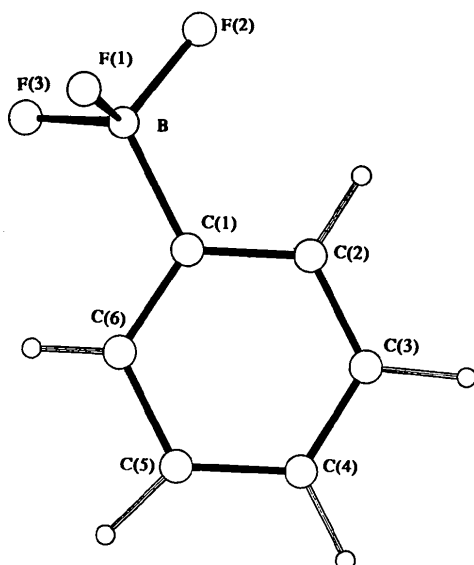


Fig. 1. The trifluorophenylborate anion.

B—F range of 1.32 (4)–1.47 (2) Å (Mhanni, Quahab, Grandjean, Amouroux & Fabre, 1991), and $[\text{C}_{11}\text{H}_9\text{N}_2\text{O}][\text{BF}_4]$, which has the four B—F bonds lying in the range 1.23 (2)–1.378 (7) Å (Sommerer, Westcott & Abboud, 1994). In the more closely related methyl derivative, $\text{K}[\text{CH}_3\text{BF}_3]$, B—F distances in the range 1.418 (2)–1.434 (2) Å have been reported (Brauer, Bürger & Pawelke, 1982). The B—C(phenyl) bond distance of B—C1 1.61 (1) Å in $\text{K}[\text{PhBF}_3]$ is comparable to the values reported for B—C(phenyl) distances in complexes containing the tetraphenylborate anion; recent examples include the sodium compound $[\text{Na}(\text{C}_{14}\text{H}_{24}\text{O}_8)][\text{BPh}_4]$ [mean B—C(phenyl) 1.652 (5) Å (Luger, Denner, Cerny, Jindrich & Trnka, 1991)] and the gold compound $[\text{Au}(\text{C}_{12}\text{H}_{27}\text{P})_2][\text{BPh}_4]$ [mean B—C(phenyl) 1.668 (17) Å (Staples, Fackler, Khan & Winpenny, 1994)].

A crystal packing diagram, viewed down the *b* axis onto the *ac* plane, showing the interaction of the trifluorophenyl anions is illustrated in Fig. 2. In the crystal, the K^+ cations lie between sheets of anionic 'squares'. Each K^+ ion is in close contact with eight surrounding F atoms, seven of which lie in the range 2.64–2.95 Å, while the eighth is further away at 3.422 (6) Å (Fig. 2*a*). Five of the F atoms surround the K^+ ion in an almost planar arrangement, with the remaining three contacts come from all three F atoms of one BF_3Ph^- anion, situated in an adjacent anionic sheet. The closest $\text{K}\cdots\text{K}$ contact distance is 4.504 (3) Å.

Fig. 2(*a*) shows that the anion sheets lie perpendicular to the *b* axis; adjacent sheets are related by 2_1 screw axes parallel to *c*. Within each sheet, anions form interlocking 'squares' which are held together by 'T-stack' π interactions. Mutually *trans* phenyl H atoms, H2 and H5 of each anion, interact with the centroids of adjacent

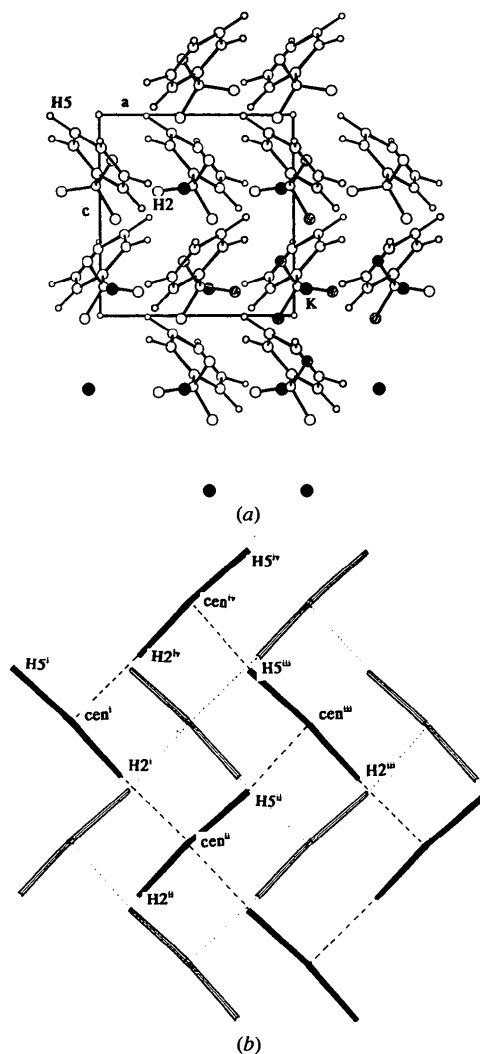


Fig. 2. (*a*) Crystal packing diagram viewed down the *b* axis onto the *ac* plane, showing part of two anionic sheets and their associated cations. The eight F atoms in close contact with one of the K^+ ions have been shaded for clarity. (*b*) Schematic representation of the anionic 'T-stack' interactions. The K^+ cations have been omitted for clarity.

perpendicular phenyl rings. Fig. 2(*b*) is a schematic representation of this 'T-stack' π interaction. Two sheets, each containing six anionic units, are shown; the top layer anions are shaded black. Fig. 2(*b*) also shows that there are essentially two independent interactions between phenyl H atoms and the π electrons: $\text{Cen}\cdots\text{H2}^i = 2.97$ Å and $\text{Cen}\cdots\text{H5}^{ii} = 2.80$ Å [Cen = centroid of the phenyl ring; symmetry code: (i) = $\frac{1}{2} - x, y, z - \frac{1}{2}$; (ii) = $x - \frac{1}{2}, y, \frac{1}{2} + z$]. There are two independent centroid-centroid contacts: $\text{Cen}\cdots\text{Cen}(-x - \frac{1}{2}, y, z + \frac{1}{2}) = 5.18$ (2) Å and $\text{Cen}\cdots\text{Cen}(-x + \frac{1}{2}, y, \frac{1}{2} + z) = 5.21$ (2) Å. The anion at equivalent position x, y, z is transformed to the second side of the square (equivalent position $\frac{1}{2} - x, y, \frac{1}{2} + z$) via a *c* glide perpendicular to the *a* axis, which in turn is related to the third side

(equivalent position 1 + x, y, z) via an *a* glide perpendicular to the *b* axis; transformation again via a *c* glide generates the fourth side (equivalent position $\frac{1}{2} - x, y, -\frac{1}{2} + z$). Opposite sides of the 'squares' are related by a unit-cell translation along the *a* and *c* axes, respectively.

The relationship between the anions is an example of an edge-to-face interaction and it has been suggested that such packing of crystalline aromatic compounds (which bring a positively polarized H atom of one aromatic group into close contact with the electron-rich π cloud of another) is energetically favourable (Burley & Petsko, 1986). This type of π interaction between aromatic groups is proving important in a range of different areas, from protein chemistry through to large macrocyclic systems (Burley & Petsko, 1985, 1986; Desiraju & Gavezzotti, 1989; Hunter & Saunders, 1990; Hunter, 1994).

Experimental

The title compound was prepared by refluxing an aqueous mixture of phenylboronic acid and potassium hydrogen fluoride. The reaction mixture was cooled to room temperature and the product was filtered and washed with small amounts of cold water; colourless crystals of the product were then recrystallized from water.

Crystal data

K ⁺ .C ₆ H ₅ BF ₃ ⁻	Mo K α radiation
$M_r = 183.94$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 25 reflections
<i>Pca</i> 2 ₁	$\theta = 8.2\text{--}10.6^\circ$
$a = 7.240 (1) \text{ \AA}$	$\mu = 0.663 \text{ mm}^{-1}$
$b = 14.373 (3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 7.444 (2) \text{ \AA}$	Rectangular block
$V = 774.6 (3) \text{ \AA}^3$	$2.43 \times 1.62 \times 0.32 \text{ mm}$
$Z = 4$	Colourless
$D_x = 1.58 \text{ Mg m}^{-3}$	

Data collection

Philips PW1100 diffractometer	494 observed reflections
$\omega/2\theta$ scans	$[I > 3\sigma(I)]$
Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)	$\theta_{\max} = 25^\circ$
837 measured reflections	$h = 0 \rightarrow 11$
494 independent reflections	$k = 0 \rightarrow 19$
	$l = 0 \rightarrow 11$
	3 standard reflections
	frequency: 300 min
	intensity decay: none

Refinement

Refinement on <i>F</i>	$(\Delta/\sigma)_{\max} = 0.01$
$R = 0.0481$	$\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$
$wR = 0.0501$	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
491 reflections	Extinction correction: none
69 parameters	Atomic scattering factors from SHELX76 (Sheldrick, 1976)
H-atom parameters not refined	
$w = 1/\sigma^2(F)$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
K	0.06242 (24)	0.59323 (15)	0.86489	0.0348 (9)
B	-0.0184 (12)	0.6354 (6)	0.3516 (19)	0.026 (5)
F(1)	0.0666 (9)	0.5751 (3)	0.2263 (10)	0.040 (3)
F(2)	0.0802 (8)	0.6201 (4)	0.5145 (9)	0.045 (4)
F(3)	-0.1983 (6)	0.6002 (3)	0.3781 (14)	0.051 (3)
C(1)	-0.0125 (11)	0.7427 (5)	0.2901 (13)	0.025 (2)
C(2)	0.1185 (10)	0.8044 (6)	0.3600 (18)	0.039 (2)
C(3)	0.1264 (13)	0.8970 (6)	0.3013 (14)	0.045 (3)
C(4)	0.0098 (16)	0.9273 (7)	0.1662 (17)	0.057 (3)
C(5)	-0.1204 (14)	0.8681 (8)	0.0928 (17)	0.056 (3)
C(6)	-0.1304 (12)	0.7757 (6)	0.1557 (14)	0.041 (2)
Cen	-0.0014 (3)	0.8359 (6)	0.2277 (16)	

Table 2. Selected geometric parameters (\AA , $^\circ$)

B—F(1)	1.41 (1)	B—F(2)	1.43 (1)
B—F(3)	1.41 (1)	B—C(1)	1.61 (1)
C(1)—C(2)	1.40 (1)	C(1)—C(6)	1.40 (1)
C(2)—C(3)	1.40 (1)	C(3)—C(4)	1.38 (2)
C(4)—C(5)	1.38 (2)	C(5)—C(6)	1.41 (2)
F(2)—B—F(1)	104.4 (7)	F(3)—B—F(1)	106.0 (7)
F(3)—B—F(2)	106.7 (9)	C(1)—B—F(1)	112.9 (9)
C(1)—B—F(2)	112.1 (7)	C(1)—B—F(3)	114.1 (7)
C(2)—C(1)—B	121.3 (8)	C(6)—C(1)—B	120.8 (8)
C(6)—C(1)—C(2)	117.7 (8)	C(3)—C(2)—C(1)	120.9 (9)
C(4)—C(3)—C(2)	120.0 (9)	C(5)—C(4)—C(3)	121 (1)
C(6)—C(5)—C(4)	119 (1)	C(5)—C(6)—C(1)	121.7 (9)

The coordinates of the K⁺ cation were deduced from a Patterson synthesis and the remaining non-H atoms were located from subsequent difference Fourier syntheses. The phenyl H atoms were located in a difference Fourier synthesis calculated using data with $\sin\theta < 0.35$. These were included in the structure-factor calculations with displacement parameters of 0.08 \AA^2 , but their parameters were not refined. The non-H atoms were assigned anisotropic displacement parameters in the final cycle of full-matrix refinement.

Data collection, cell refinement and data reduction: PW1100 software. Structure solution and refinement: SHELX76 (Sheldrick, 1976). Molecular graphics: ORTEPII (Johnson, 1976). Preparation of material for publication: PUBTAB (Henrick, 1982).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and intermolecular distances involving H atoms have been deposited with the IUCr (Reference: NA1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaqua[2,13-dimethyl-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene]magnesium(II) Diperchlorate

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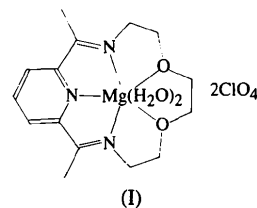
Abstract

The O and N atoms of the macrocyclic ligand occupy the pentagonal sites and the aqua O atoms the apical sites of the pentagonal bipyramidal geometry at the seven-coordinate Mg atom of the title compound, $[\text{Mg}(\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$. Each H_2O molecule is involved in hydrogen bonding with the two ClO_4^- ions [2.797 (7) and 2.963 (9) Å].

Comment

The study of the title complex, diaqua[2,13-dimethyl-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),-2,12,14,16-pentaene]magnesium(II) diperchlorate, (I), was undertaken as an extension of a study of the effect of metal ions in promoting the synthesis of 2,13-dimethyl-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, a relatively

rigid macrocycle that can be isolated only as its metal complexes (Drew, Othman, McFall, McIlroy & Nelson, 1977).



The magnesium complex of the macrocycle was assigned pentagonal bipyramidal geometry (Cook, Fenton, Drew, McFall & Nelson, 1977) and this has been confirmed in the present study. The cationic complex has exact twofold symmetry with the Mg, N and C3 atoms lying on the twofold axis that relates one half of the cation to the other.

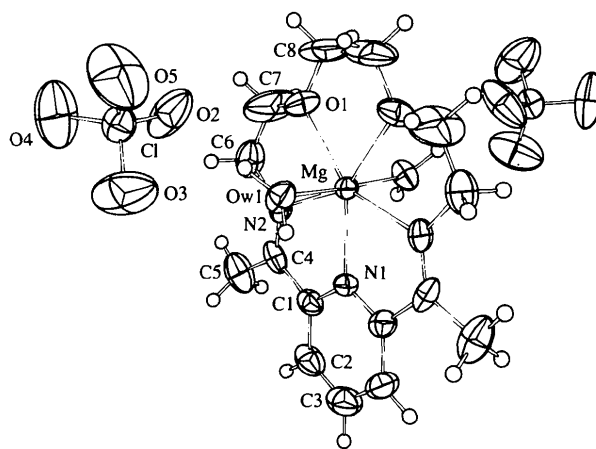


Fig. 1. ORTEPII (Johnson, 1976) plot of the title complex with displacement ellipsoids plotted at the 40% probability level.

Experimental

The title compound was synthesized from magnesium perchlorate, 2,6-diacetylpyridine and 1,8-diamino-3,6-dioxaoctane, according to the method of Cook, Fenton, Drew, McFall & Nelson (1977). Recrystallization from methanol gave yellow octahedral crystals.

Crystal data

$[\text{Mg}(\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$
 $M_r = 534.59$
 Monoclinic
 $C2/c$
 $a = 15.964 (3) \text{ \AA}$
 $b = 13.603 (1) \text{ \AA}$
 $c = 10.835 (2) \text{ \AA}$
 $\beta = 97.000 (7)^\circ$
 $V = 2335.5 (6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.520 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 1-25^\circ$
 $\mu = 0.370 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Octahedral
 $0.29 \times 0.29 \times 0.29 \text{ mm}$
 Yellow