

Structure of Potassium Hydrogen Bis(*p*-fluorobenzoate)

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Abstract. $K^+ \cdot C_{14}H_9F_2O_4^-$, $M_r = 318.32$, monoclinic, $C2/c$, $a = 32.337$ (7), $b = 3.817$ (2), $c = 11.239$ (2) Å, $\beta = 107.42$ (2)°, $V = 1323.6$ Å³, $Z = 4$, $D_c = 1.60$, $D_o = 1.59$ Mg m⁻³, $R = 0.052$ for 731 reflections with $|F_o| > 6\sigma(F_o)$. The acidic H atoms appear to be located on centres of symmetry, and link pairs of *p*-fluorobenzoate residues together by a strong symmetrical hydrogen bond ($O \cdots O' = 2.460$ Å, $O \cdots H \cdots O' = 180^\circ$).

Introduction. The present structure was determined as part of a series of studies on compounds exhibiting strong hydrogen bonding (Miller, Kanippayoor, Clark & Emsley, 1979; Emsley, Jones, Miller, Overill & Waddilove, 1981; Clark, Kanippayoor & Miller, 1981). Crystals were supplied by Professor James Clarke, York University, England. A crystal $0.015 \times 0.10 \times 0.52$ mm was aligned about the needle (*b*) axis. Weissenberg photographs revealed the absence of *hkl* reflections for (*h* + *k*) odd, and of *h0l* reflections for *l* odd. The space group is *Cc* or *C2/c*. Unit-cell dimensions were determined from 13 accurately centred reflections ($33.0^\circ < 2\theta < 45^\circ$) on a Nonius CAD-4 diffractometer using graphite-monochromatized Mo *K* α radiation ($\lambda = 0.71069$ Å). The data collection conditions were: ω - 2θ scan, ω scan width (°) $0.70 + 0.35 \times \tan\theta$, $\theta_{\min} = 1$, $\theta_{\max} = 25^\circ$, 3 mm aperture, maximum ω scan speed 2° min^{-1} , maximum scan time 600 s, background counted one quarter of the scan time at each end of the scan. A standard intensity was measured every hour, and the orientation checked after every 100 measured reflections. There was no significant variation in the standard during the data collection. A total of 2803 reflections (three quarters of data) were measured. The equivalent reflections were averaged to yield 1176 unique values; of these, 731 had $F > 6\sigma(F)$ and were classified as observed. Intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. No absorption correction was made ($\mu = 0.442 \text{ mm}^{-1}$).

The structure was initially solved in space group *Cc* with *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by

Table 1. Atomic parameters for $KH(p\text{-FC}_6\text{H}_4\text{CO}_2)_2$

E.s.d.'s are in parentheses. $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
K	0.0	0.1562 (4)	0.25	0.0507 (5)
F	-0.23468 (6)	0.1236 (9)	-0.1096 (2)	0.065 (1)
C(1)	-0.12262 (11)	0.3857 (11)	0.0046 (4)	0.035 (1)
C(2)	-0.16561 (11)	0.3292 (13)	0.0003 (4)	0.038 (1)
C(3)	-0.19286 (11)	0.1849 (13)	-0.1064 (4)	0.040 (1)
C(4)	-0.18056 (11)	0.0955 (11)	-0.2080 (4)	0.040 (1)
C(5)	-0.13753 (11)	0.1538 (12)	-0.2029 (3)	0.034 (1)
C(6)	-0.10873 (11)	0.2940 (11)	-0.0968 (3)	0.029 (1)
C(7)	-0.06295 (11)	0.3576 (12)	-0.0956 (3)	0.034 (1)
O(1)	-0.03639 (7)	0.4521 (9)	0.0103 (2)	0.048 (1)
O(2)	-0.05204 (8)	0.3220 (9)	-0.1909 (2)	0.043 (1)

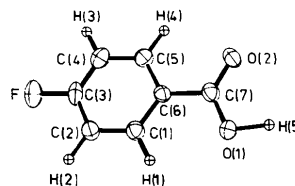


Fig. 1. ORTEP plot (Johnson, 1976) of the asymmetric unit of the centrosymmetric $[H(FC_6H_4CO_2)_2]^-$ anion.

Table 2. Distances (Å) and angles (°) in $KH(p\text{-FC}_6\text{H}_4\text{CO}_2)_2$

C(1)–C(2)	1.393 (5)	C(3)–F	1.362 (4)
C(2)–C(3)	1.373 (6)	C(7)–O(1)	1.293 (4)
C(3)–C(4)	1.360 (6)	C(7)–O(2)	1.231 (4)
C(4)–C(5)	1.393 (5)	O(1)–H(5)	1.230 (2)
C(5)–C(6)	1.382 (5)	K–O(1)	2.832 (3)
C(6)–C(1)	1.389 (5)	K–O(2 ⁱⁱ)	2.697 (3)
C(6)–C(7)	1.496 (5)	K–O(2)	2.812 (3)
C(6)–C(1)–C(2)	119.8 (4)	O(1)–C(7)–O(2)	123.1 (3)
C(1)–C(2)–C(3)	117.7 (4)	H(5)–O(1)–C(7)	110.3 (3)
C(2)–C(3)–C(4)	124.1 (3)	O(1)–K–O(1 ⁱⁱⁱ)	133.0 (3)
C(2)–C(3)–F	117.7 (4)	O(2)–K–O(2 ^v)	177.5 (3)
C(4)–C(3)–F	118.2 (4)	O(1)–K–O(2)	66.4 (3)
C(3)–C(4)–C(5)	117.7 (4)	O(1)–K–O(2 ⁱⁱ)	98.5 (3)
C(4)–C(5)–C(6)	120.3 (4)	O(1)–K–O(2 ^{iv})	80.5 (3)
C(5)–C(6)–C(1)	120.3 (3)	O(1)–K–O(2 ^v)	113.1 (3)
C(5)–C(6)–C(7)	118.7 (3)	O(2)–K–O(2 ⁱⁱ)	87.7 (3)
C(1)–C(6)–C(7)	120.9 (3)	O(2)–K–O(2 ^{iv})	89.8 (3)
O(1)–C(7)–C(6)	115.9 (3)	O(2 ⁱⁱ)–K–O(2 ^v)	94.8 (3)
O(2)–C(7)–C(6)	121.0 (3)		

Symmetry superscripts: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $-x, y + 0.5, -z$; (iv) $x, 1-y, 0.5+z$; (v) $x, -y, 0.5+z$.

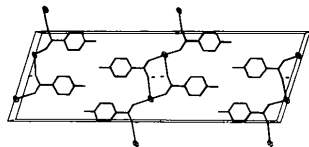


Fig. 2. Unit-cell contents of $\text{KH}(\text{p-FC}_6\text{H}_4\text{CO}_2)_2$. Dashed lines indicate hydrogen bonds.

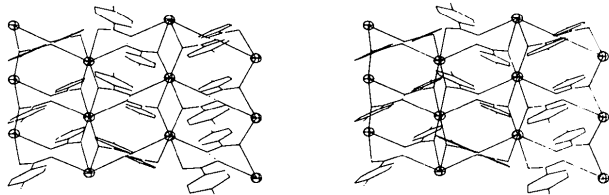


Fig. 3. One of the bands parallel to (100), showing how the K^+ ions link the carboxylate residues. The c and b axes are horizontal and vertical, respectively.

full-matrix least-squares with the *SHELX* set of programs (Sheldrick, 1976). As refinement proceeded it became apparent that the correct space group was $C2/c$, and refinement was completed in this group. Scattering factors for neutral C, H, F, O, and K were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $w = [\sigma^2(F_o) + 0.0002 F_o^2]^{-1}$ and $\sigma(F_o)$ is the standard deviation based on counting statistics. All non-H atoms were given anisotropic temperature factors. The positions of the phenyl H atoms were calculated with $r_{\text{C-H}} = 1.08 \text{ \AA}$ and assigned isotropic thermal parameters U of 0.06 \AA^2 . The final weighted residual, $R_w = (\sum \Delta^2 / \sum w F_o^2)^{1/2}$, was 0.045 for the observed reflections and 0.057 for all reflections. There were no significant features on the final difference map (highest peak 0.25 e \AA^{-3}).

The atomic positional parameters are presented in Table 1, and the numbering scheme is shown in Fig. 1.* Bond distances and angles are given in Table 2. The molecular packing is shown in Figs. 2 and 3.

Discussion. The structure consists of potassium ions and $[\text{H}(\text{FC}_6\text{H}_4\text{CO}_2)_2]^-$ anions (Fig. 2). Each $\text{p-FC}_6\text{H}_4\text{CO}_2^-$ anion is linked to another across a centre of symmetry by a short, strong hydrogen bond. The atom H(5) appears to lie on a centre of symmetry between O(1) and the centrosymmetrically related O(1'). However, the possibility of a disordered O—H...O system cannot be ruled out, as slight displacement of the H atom from the centre of symmetry cannot be determined accurately by X-ray methods.

* Lists of structure factors, H parameters, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36876 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The O(1)...O(1') distance of $2.460(4) \text{ \AA}$ is comparable to values of $2.435\text{--}2.488 \text{ \AA}$ reported for other monocarboxylates which exhibit strong hydrogen bonding (Emsley, 1980).

The phenyl ring is planar, with the carboxylate group twisted slightly out of the phenyl plane (8.9°). The potassium ions are located on crystallographic twofold axes and are surrounded by six carboxylate O atoms, two O(1) and four O(2) atoms from different $\text{p-FC}_6\text{H}_4\text{CO}_2^-$ anions. Each O(1) atom thus takes part in the hydrogen bond and one contact to K^+ , whereas each O(2) is involved in two contacts to K^+ . The four O(2) contacts form a nearly regular square plane about each K^+ . Coordination is completed by two O(1) atoms so that a highly distorted octahedron is formed (Table 2). The average K—O distance is $2.78(4) \text{ \AA}$, which is typical for six-coordinate potassium (McGregor, Speakman & Lehmann, 1977). Irregular coordination of alkali-metal ions is quite frequently found in structures such as the present one, where hydrogen-bonding interactions are as important as the usual ionic bonding in determining the overall structure (McGregor *et al.*, 1977; Perotti & Tazzoli, 1981).

The overall structure consists of thick bands parallel to the (100) plane (Fig. 3). They result from linking the $[\text{H}(\text{p-FC}_6\text{H}_4\text{CO}_2)_2]^-$ anions by K^+ ions. The centre of each band is polar and contains the carboxylate moieties and K^+ ions. Contacts between bands are nonpolar and are limited to van der Waals F...F and F...C contacts.

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