

## Structure of Caesium Fluoride–Succinic Acid (1:1), $\text{CsF}\cdot\text{C}_4\text{H}_6\text{O}_4$

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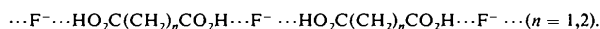
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**Abstract.**  $M_r = 270.0$ , orthorhombic, space group  $Pbnm$ ,  $a = 6.078$  (1),  $b = 7.386$  (1),  $c = 17.419$  (2) Å,  $U = 782.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.293$  g cm<sup>-3</sup>,  $F(000) = 504$ ,  $\mu(\text{Mo } K\alpha) = 44.20$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å, room temperature,  $R = 0.038$  for 904 reflections with  $I \geq 2\sigma(I)$ . The structure consists of chains of alternate succinic acid molecules and  $\text{F}^-$  ions linked through very short hydrogen bonds,  $R(\text{O}\cdots\text{F}) = 2.449$  (6) Å.

**Introduction.** Whereas a large amount of structural data describing compounds with short  $\text{F}\cdots\text{F}$ ,  $\text{O}\cdots\text{O}$  and even  $\text{N}\cdots\text{N}$  hydrogen bonds is available, relatively little has been published on heteronuclear hydrogen-bonded compounds and, in particular, on solids containing  $\text{O}\cdots\text{F}$  hydrogen bonds (Emsley, 1980). Examples of this type include the  $\text{O}\cdots\text{F}$  bonds in  $\text{KH}_2\text{PO}_3\cdot\text{HF}$  (Altenburg & Mootz, 1971), those in the metal fluoride hydrates (Simonov & Bukvetsky, 1978) and those of the HF hydrates (Mootz, Ohms & Poll, 1981).

In our studies of the adducts formed between dicarboxylic acids and alkali-metal fluorides we have determined the structures of  $\text{KF}\cdot(\text{CH}_2\text{CO}_2\text{H})_2$  (Emsley, Jones, Osborn & Overill, 1982), of its  $d_2$ -deuterated derivative (Emsley, Jones & Kuroda, 1981), and of  $\text{KF}\cdot\text{CH}_2(\text{CO}_2\text{H})_2$  (Emsley, Jones & Kuroda, 1982). In each case the acid molecules are linked to  $\text{F}^-$  ions by very short  $\text{O}\cdots\text{F}$  hydrogen bonds forming an infinite chain structure:



In the adduct  $\text{KF}\cdot(\text{CH}_2\text{CO}_2\text{H})_2$  the hydrogen bond is highly asymmetric. On deuteration the  $R(\text{O}\cdots\text{F})$  bond length stays at a similar distance of 2.445 (3) Å, compared to 2.441 (3) Å in the protonated bond.

In the malonic acid adduct,  $\text{KF}\cdot\text{CH}_2(\text{CO}_2\text{H})_2$ , there is a range of hydrogen bonds of lengths between 2.41 (4) and 2.49 (4) Å. The H atoms could not be

located with certainty, although infrared evidence suggests two kinds of proton environment (Jones, 1982).

The present work was undertaken to investigate the effect of a change of metal ion on the structure and, in particular, on the geometry of the  $\text{O}\cdots\text{F}$  hydrogen bond. Caesium fluoride was chosen to demonstrate any such effect since the  $\text{Cs}^+$  ionic radius (1.70 Å) is considerably larger than that of  $\text{K}^+$  (1.38 Å) (Shannon & Prewitt, 1969).

**Experimental.** Crystals of  $\text{CsF}\cdot(\text{CH}_2\text{CO}_2\text{H})_2$  were prepared by evaporation of an aqueous solution of caesium fluoride and succinic acid in equimolar (1:1) amounts; composition: found: C 17.78, H 2.43, F 6.37%; calculated for  $\text{C}_4\text{H}_6\text{CsFO}_4$ : C 17.78, H 2.20, F 7.04%; loss of HF and/or absorption of  $\text{H}_2\text{O}$  is probably responsible for the slight discrepancy. Intensities collected on an Enraf–Nonius CAD-4 diffractometer using a crystal of approximate dimensions 0.4 × 0.4 × 0.4 mm mounted about  $c$ ;  $\theta$ – $2\theta$  scans; cell parameters obtained from 25 well centred reflections. After correction for Lorentz and polarization factors and averaging of equivalent reflections, there remained 1013 unique reflections ( $\theta_{\text{max}} = 30^\circ$ ). Although the space group cannot be uniquely determined from extinctions the centrosymmetric space group  $Pbnm$ † was more likely than the alternative  $Pbn2_1$  by comparison with the previously determined potassium analogue, where the symmetry is described by the former space group. Structure determined using *SHELX76* (Sheldrick, 1976); convergence of atomic parameters rapid in  $Pbnm$ , consequently this space group was used throughout; anisotropic refinement of all non-hydrogen atoms gave  $R = 0.051$ ; H atoms then located from a difference Fourier map; isotropic refinement of these in subsequent least-squares cycles led to a final  $R = 0.038$  for 904 reflections with  $I > 2\sigma(I)$ ; unit weights.

† Non-standard setting of  $Pnma$  (No. 62); equivalent positions:  $\pm(x, y, z)$ ;  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ;  $\bar{x}, \bar{y}, \frac{1}{2}+z$ ;  $\frac{1}{2}+x, \frac{1}{2}-y, z$ .

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Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

The numbering of the atoms is the same as in Emsley, Jones, Osborn & Overill (1982) and Emsley, Jones & Kuroda (1981).

	x	y	z	$U_{eq}/U$
Cs	5667 (1)	2601 (1)	7500	34 (0)*
F	633 (9)	3742 (7)	7500	41 (3)*
O(1)	1389 (8)	2714 (7)	6189 (3)	51 (2)*
O(2)	-1332 (8)	724 (6)	6315 (3)	51 (3)*
C(1)	139 (10)	1384 (8)	5934 (3)	35 (3)*
C(2)	696 (11)	790 (8)	5131 (3)	36 (3)*
H(1)	892 (106)	3044 (90)	6792 (38)	47 (19)
H(21)	391 (130)	1751 (109)	4898 (46)	69 (24)
H(22)	2315 (156)	255 (110)	5270 (40)	78 (26)

$$* U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

F-H(1)	1.35 (6)	C(1)-C(2)	1.504 (7)
F-O(1)	2.449 (6)	C(2)-H(21)	0.84 (8)
H(1)-O(1)	1.12 (6)	C(2)-H(22)	1.09 (9)
C(1)-O(1)	1.319 (7)	C(2)-C(2 <sup>i</sup> )	1.512 (12)
C(1)-O(2)	1.216 (8)		
H(1)-O(1)-C(1)	109 (3)	H(22)-C(2)-C(1)	96 (4)
C(2)-C(1)-O(1)	113.6 (5)	H(21)-C(2)-H(22)	128 (7)
C(2)-C(1)-O(2)	123.4 (5)	H(1)-F-H(1 <sup>ii</sup> )	133 (6)
O(1)-C(1)-O(2)	123.0 (5)	O(1)-F-O(1 <sup>ii</sup> )	138 (1)
H(21)-C(2)-C(1)	99 (5)	O(1)-H(1)-F	167 (6)

## Geometry at Cs

Cs-O(2 <sup>iii</sup> ), O(2 <sup>iv</sup> )	3.083 (5)
Cs-O(2 <sup>v</sup> ), O(2 <sup>vi</sup> )	3.122 (5)
Cs-F <sup>vii</sup> , F	2.958 (6), 3.134 (6)

Closest hydroxyl oxygen: Cs...O(1) 3.462 (5)

## Symmetry code

(i) $-x, -y, 1-z$	(v) $\frac{1}{2}-x, \frac{1}{2}+y, z$
(ii) $x, y, \frac{3}{2}-z$	(vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$
(iii) $1+x, y, z$	(vii) $\frac{1}{2}-x, y, -\frac{1}{2}z$
(iv) $1+x, y, \frac{3}{2}-z$	

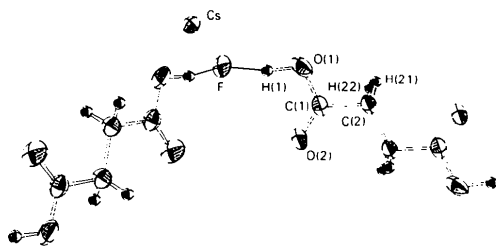


Fig. 1. The structure of the fluoride-succinic acid chains of  $\text{CsF} \cdot (\text{CH}_2\text{CO}_2\text{H})_2$ .

**Discussion.** Atomic coordinates are given in Table 1,\* and bond lengths and angles in Table 2.

The structure of  $\text{CsF} \cdot (\text{CH}_2\text{CO}_2\text{H})_2$  is identical with that of the potassium analogue in that  $\text{F}^-$  and metal ions occupy special positions on the mirror planes and succinic acid molecules lie across centres of symmetry in such a way that infinite hydrogen-bonded chains are formed (Fig. 1). However, the unit-cell volume is substantially greater in the present case, such an increase being necessary to accommodate the large  $\text{Cs}^+$  ion. On the other hand, the lengths of the two hydrogen bonds to each  $\text{F}^-$  ion have been almost unaffected by the change in cation:  $R(\text{O} \cdots \text{F}) = 2.449 (6)$  (Cs adduct);  $R(\text{O} \cdots \text{F}) = 2.441 (3) \text{\AA}$  (K adduct). There is a slight expansion of the  $\text{C}(1)-\text{O}(1)$  bond by  $0.014 \text{\AA}$  which is consistent with a marginally weaker  $\text{O} \cdots \text{F}$  hydrogen bond in  $\text{CsF} \cdot (\text{CH}_2\text{CO}_2\text{H})_2$ . Moreover, within the hydrogen bonds the asymmetry of the protons is less pronounced in the caesium adduct;  $\text{F}-\text{H}(1) = 1.60 (3)$  and  $\text{H}(1)-\text{O}(1) = 0.85 (3) \text{\AA}$  in the potassium case.

Clearly, the structure of  $\text{CsF} \cdot (\text{CH}_2\text{CO}_2\text{H})_2$  places it in the category of crystals containing the rare  $\text{O} \cdots \text{F}$  hydrogen bonds with short internuclear distances.

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38430 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- ALTENBURG, H. & MOOTZ, D. (1971). *Acta Cryst.* **B27**, 1982-1986.
- EMSLEY, J. (1980). *Chem. Soc. Rev.* **9**, 91-124.
- EMSLEY, J., JONES, D. J. & KURODA, R. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2141-2143.
- EMSLEY, J., JONES, D. J. & KURODA, R. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1179-1184.
- EMSLEY, J., JONES, D. J., OSBORN, R. S. & OVERILL, R. E. O. (1982). *J. Chem. Soc. Dalton Trans.* pp. 809-813.
- JONES, D. J. (1982). PhD thesis, Univ. of London.
- MOOTZ, D., OHMS, U. & POLL, W. (1981). *Z. Anorg. Allg. Chem.* **479**, 75-83.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925-946.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SIMONOV, V. I. & BUKVETSKY, B. V. (1978). *Acta Cryst.* **B34**, 355-358.