A Very Short, Very Asymmetrical O–H··F⁻ Hydrogen Bond in KF·$(CH_2CO_2H)_2$; *X*-Ray Crystal Structure

By JOHN EMSLEY* and DEBORAH J. JONES,
(*Department of Chemistry, King's College, Strand, London* WC2R 2LS)
and RUTH S. OSBORN
(*Department of Chemistry, X-Ray Crystallography Section, Imperial College of Science and Technology, South Kensington, London* SW7 2AY)

Summary A new 1:1 adduct of KF and succinic acid has been prepared and its crystal structure, determined by the heavy atom method, reveals an unexpectedly short hydrogen bond with O . . . F = 2·440(4) Å.

POTASSIUM FLUORIDE is very soluble in simple carboxylic acids[1] and the solutions are noted for their unusual physical,[2] chemical,[3] and spectroscopic[4] properties which have been explained as arising from the formation of very strong hydrogen bonds, of the type RCO_2–H–F^-. Solvates KF·$2RCO_2H$ and KF·RCO_2H can be obtained from such solutions but not as single crystals suitable for *X*-ray crystallography.

Theoretical calculations[5] on HCO_2–H–F^- and CH_3CO_2–H–F^- suggested short hydrogen bonds, O . . . F^- = 2·38 Å, with the proton sited appreciably nearer the fluoride ion than its parent oxygen. Because of this the calculated bond energy is defined with respect to RCO_2^- + HF, and is 105 kJ mol^{-1}, rather than with respect to RCO_2H + F^-, in which case it would be 250 kJ mol^{-1}.[6]

We now report the adduct KF·$(CH_2CO_2H)_2$, crystals of which have been grown from an *aqueous* solution of KF and succinic acid. Single crystals have been investigated by *X*-ray diffraction and reveal conclusively that very short hydrogen bonds are formed between fluoride ions and carboxylic acid groups.

Crystal data: The colourless crystals of KF·$(CH_2CO_2H)_2$, m.p. 153 °C, are orthorhombic, space group *Pnam*, a = 7·0680(1), b = 5·5710(1), c = 16·846(2) Å; U = 663·3 $Å^3$; Z = 4; D_c = 1·764 g cm^{-3}. Intensity data were collected to a maximum θ of 70° using a Siemens off-line 4-circle diffractometer. Of the 651 reflections thus measured 14 were classified as unobserved.[7] The data were processed in the usual way[8] and the structure was solved by the heavy atom method and refined to give a current R factor of 0·046. Full details of bond length and angles are not given here except for the region of the fluoride ion, whose environment is shown in the Figure.† The K and F atoms lie on crystallographic mirror planes and the succinic acid molecules lie across centres of symmetry. The crystal

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

consists mainly of a hydrogen-bonded polymer of alternate fluoride and succinic acid units

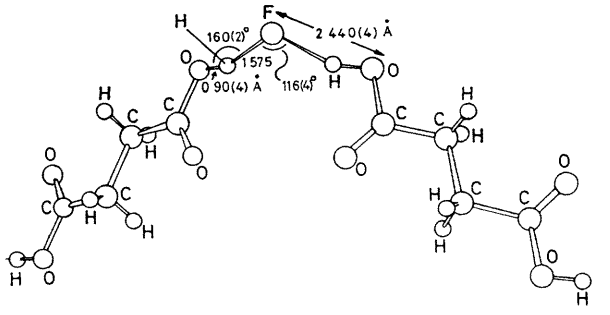

FIGURE The very short hydrogen bonds in KF $(CH_2CO_2H)_2$

Relatively few systems display O–H–F hydrogen bonding and only a small number of crystals, chiefly metal fluoride hydrates, display this type of bond Generally these hydrogen bonds have lengths O F in the range 2 56–2·86, with an average value of 2·68 Å [9] The shortest O–H–F bond of this kind is 2·56 Å in $RbVF_4\ 2H_2O$ [10] The shortest O–H–F bond so far reported is 2·38 Å in $KH_2PO_3\ HF$ [11] This is an asymmetric bond with ∠OHF 145° and with the proton located close to its parent fluorine

KF $(CH_2CO_2H)_2$ has short asymmetric hydrogen bonds with each fluoride ion acting as an acceptor to two carboxylic protons, a situation which is suggested by nuclear Overhauser effect studies on KF in $MeCO_2H$ solution [12] Moreover, and at variance with the theoretical predictions, the hydrogen bonding protons are located near the parent oxygens These hydrogen bonds are, by virtue of their shortness, undoubtedly of the single minimum potential-well type and unlike most bonds of this kind the well is very asymmetric

The authors thank D J Williams for helpful discussion and the S R C for a studentship (to D J J)

(*Received, 28th April* 1980, *Com.* 444.)

[1] J Emsley, *J Chem Soc* (*A*), 1971, 2511
[2] J Emsley, *J Chem Soc* (*A*), 1971, 2702
[3] J H Clark and J Emsley, *J Chem Soc , Dalton Trans* , 1975, 2129, O P A Hoyte, *J Chem Soc , Perkin Trans* 1, 1977, 1091
[4] J H Clark and J Emsley, *J Chem Soc , Dalton Trans* , 1973, 2154
[5] J Emsley, O P A Hoyte, and R E Overhill, *J Chem Soc , Perkin Trans* 2, 1977, 2079
[6] W J Bouma and L Radom *Chem Phys Lett* , 1979 **64**, 216, J Emsley and R E Overhill, *ibid* , 1979, **65**, 616
[7] F H Allen, D Robers, and P G H Troughton, *Acta Crystallogr Sect B*, 1971, **27**, 1325
[8] J M Stewart, University of Maryland Technical Report TR646 Revised Version, 1972
[9] V I Simonov and B V Bukvetsky, *Acta Crystallogr , Sect B*, 1978, **34** 355
[10] B V Bukvetsky, L A Muradyan R L Davidovich, and V I Simonov, *Sov J Coord Chem* , 1976, **2**, 869
[11] H Altenburg and D Mootz, *Acta Crystallogr , Sect B*, 1971, **27**, 1982
[12] J M Miller, R K Kanippayoor, J H Clark, and J Emsley, *J Chem Soc , Chem Commun* , 1979, 758