X-Ray Crystal Structure of Caesium Hydrogen Bis(Monofluorosulphate), $Cs^+[O_2FSO.H.OSFO_2]^-$, with a Very Short Hydrogen Bond

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Summary X-ray diffraction provides the first evidence for the existence of the homoconjugated anion $[O_2FSO.H.OSFO_2]^-$ containing a very short and symmetrical hydrogen bond [O···O = 2·41(1) Å].

THE title compound was prepared by reaction of CsCl with an excess of HSO_3F (80 mol%). The solution was heated to 100 °C, then cooled very slowly to ambient temperature to yield colourless single crystals which were separated from the solution and washed with dry CCl_4. The crystals were extremely hygroscopic and, in a dry box, only one of them could be mounted without decomposition in a Lindemann glass capillary tube to be analysed by *X*-ray crystallography.†

Crystal data: $CsH(SO_3F)_2$, $M = 332$, monoclinic, space group $C2/c$, $a = 13{\cdot}359(3)$, $b = 7{\cdot}724(1)$, $c = 10{\cdot}540(3)$ Å, $\beta = 135{\cdot}17(2)°$, $Z = 4$, $D_m = 2{\cdot}88$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) =$

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† A Cs^+ cation was used because a large non-polarising cation was necessary for the symmetrical, short hydrogen bonds to be observed. It was not possible to obtain stable high-melting (>40 °C) compounds with a large organic cation.

54·8 cm^{-1}. Intensity data were collected by the ω–θ scan technique on a Nonius CAD 4 diffractometer ($2 \leqslant 2\theta \leqslant 50°$); 618 unique reflexions were obtained with $I > 3\sigma(I)$. The structure was solved by Patterson synthesis and refined by full-matrix least-squares to a final R of 4·4% with anisotropic thermal parameters. The structure is shown in the Figure.‡

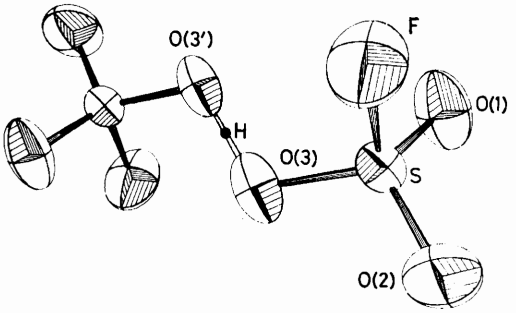

FIGURE. The anion $(O_2FSO.H.OSFO_2)^-$ in $CsH(SO_3F)_2$.

The homoconjugated anion $[O_2FSO.H.OSFO_2]^-$ is centrosymmetric, the fluorosulphate groups being related to each other through a crystallographic inversion centre 4(b) and linked *via* hydrogen bonding through the hydrogen atom which most probably lies on this inversion centre or, less probably, is disordered around it, since the hydrogen atom could not be localized on the final Fourier difference map. The hydrogen bond is one of the shortest ever reported [O···O = 2·41(1) Å] for homoconjugated anions of very strong acids. The hydrogen bond is even shorter than the symmetrical one reported by Roziere *et al.*[1] in the analogous caesium hydrogen dinitrate system [O···O = 2·468(8) Å]. Another short, although asymmetrical, hydrogen bond [O···O = 2·434(4) Å] was recently reported for $Na_3H(SO_4)_2$ by Catti *et al.*[2] So far, no structural data have been given for the $H(SO_3F)_2^-$ anion, although the existence of such a symmetrical anion was suggested by Vast *et al.*[3] in the solvate $NaSO_3F$–HSO_3F using Raman techniques and by us[4] for the compounds Brpy–$2HSO_3F$ (Brpy = 3-bromopyridine) and Bipy–$4HSO_3F$ (Bipy = 2,2′-bipyridyl). The anion described here does not exhibit the highest symmetry $C2/h$ which would be satisfied with the fluorine atoms lying in the plane of the hydrogen bond S–O(3)–H–O(3′); in fact, the fluorine atoms are nearly perpendicular to this plane [dihedral angle of 94·5° between the planes S–O(3)–H–O(3′) and F–S–O(3)], restricting the symmetry of this anion to C_i.

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‡ The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

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