

Neutron diffraction study of the HF adducts containing a hydrogen bond F–H···O

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Received 8 January 2004; received in revised form 3 June 2004; accepted 4 June 2004

Available online 15 July 2004

Abstract

Single-crystal structures of HF adducts of acid salts $\text{CsH}_2\text{PO}_3 \cdot \text{HF}$, $\text{KH}_2\text{PO}_4 \cdot \text{HF}$, and $\text{CsH}_2\text{PO}_4 \cdot \text{HF}$ were determined by neutron diffraction using the Laue method. In the crystals, HF molecules are connected to anions by means of new type of hydrogen bonds, F–H···O, which are significantly shorter (F···O distances 2.356–2.386(3) Å) than strong O–H···O or O–H···F hydrogen bonds. The H–F distances in the structures of these adducts, 1.020–1.027(5) Å, are compared with those in crystalline HF and hydrofluoride anions.

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Keywords: Hydrogen fluoride; Hydrogen bond; Neutron diffraction

1. Introduction

The chemical behavior of hydrogen fluoride, HF, in combination with different salts in water solution depends on factors such as the nature of the salt, overall and relative concentration of reagents, etc. Alkali metal fluorides in concentrated HF solutions give rise to acid fluorides of typical composition $M(\text{H}_n\text{F}_{n+1})$. Some oxosalts are able to react with HF to form anion mixed hydrogen salts, e.g., $M_2(\text{NO}_3)(\text{HF}_2)$ ($M = \text{K}, \text{NH}_4$) [1]. In dilute solutions, HF converts to hydroxonium fluorides [2] due to its more acidic nature compared with water. In more concentrated water solutions of acid oxosalts and HF, formation of HF adducts with general composition $M\text{H}_2\text{XO}_y \cdot z\text{HF}$ is possible, as documented for some phosphites, phosphates, sulfates, and selenates [3–5]. A general structural feature of these HF adducts is the presence of a previously unknown type of strong hydrogen bond, F–H···O. Single-crystal X-ray structure

investigations of seven compounds of this type revealed F···O distances ranging from 2.35 to 2.38 Å [3–5]. Although the position of H atoms could be determined in these X-ray studies, neutron diffraction (with its much better resolution of H atoms) was ultimately required to validate and properly characterize this new type of hydrogen bond.

In the present study, single crystals of three HF adducts were studied by neutron diffraction using the white-beam Laue method with cylindrical image plates. The results obtained are discussed and compared with previously published X-ray data.

2. Experimental

Adducts of oxosalts with HF were prepared according to Refs. [4,5]. The adducts $\text{CsH}_2\text{PO}_3 \cdot \text{HF}$, $\text{KH}_2\text{PO}_4 \cdot \text{HF}$ and $\text{CsH}_2\text{PO}_4 \cdot \text{HF}$ were obtained as single-crystal samples with linear dimensions 0.5–4 mm. The crystals are not stable in air in the presence of mother liquor. They are, however, relatively stable as dried solids, slowly losing HF over the course of several hours. For the single-crystal experiment, crystals with edge

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dimensions of 1–2 mm were extracted from solution, dried with filter paper, glued on the Al sample holder and placed in a standard ‘Orange’ cryostat, all within 5–10 min. Below 240–250 K, the crystals are stable towards the loss of HF, and the cryostat could be evacuated before further cooling.

Neutron diffraction measurements were carried out on the Very Intense Vertical Axis Laue Diffractometer (VIVALDI) at the Institut Laue–Langevin (ILL) in Grenoble, France. This instrument uses a polychromatic (‘white’) neutron beam, and records diffracted intensities on a cylindrical image plate. For each sample, 5–7 exposures of 60–100 min each were recorded, separated by 20–30° rotations of the vertical (ϕ) axis.

Data processing was carried out using the CCP4 Laue Suite [6]. Image plates were oriented and indexed on the basis of symmetries and unit cell parameters obtained in the previous X-ray study, and the unit cell and diffractometer parameters were refined (note that due to the use of a polychromatic neutron beam, only *relative* unit cell parameters could be refined). After integration, symmetrically equivalent reflections recorded at different positions (i.e., diffracted at different wavelengths) were used to determine the intensity vs. wavelength function of the polychromatic beam. Integrated intensities were normalized to this function.

The data sets obtained were used for structure refinement with the program SHELXL97 [7]. Starting atomic coordinates were taken from the previous X-ray study and neutron scattering lengths were taken from [8]. Unit cell parameters were modified to take into account the lower temperatures used for the VIVALDI study compared with the corresponding X-ray study. Anisotropic atomic displacement parameters were refined for all atoms including hydrogen. Crystallographic

parameters and some details of structure refinements are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and discussion

The use of the white-beam Laue method with VIVALDI allowed the necessary neutron diffraction data sets to be collected within 6–12 h, comparable to data collection times using modern X-ray diffractometers. Despite this rapid data collection, the accuracy of the final structure determinations is virtually the same as that obtained using X-rays for the non-hydrogen atoms, and much higher for the protons themselves. A comparison of results of this neutron diffraction study with those of the X-ray investigation on the same three compounds [4,5] showed good correspondence for all non-hydrogen atoms, but the positions for hydrogen atoms (protons) were significantly corrected. Consequently, greater attention will be paid below to the description and discussion of hydrogen bonds, with other features of the structure presented only briefly.

A common feature of the three structures of the HF adducts is the presence of alkali metal cations, hydrogen bonded polymeric anions to which HF molecules are attached via F–H...O bonds. In the structure of CsH₂PO₃·HF (I), the Cs cation is surrounded by 5O and 4F atoms at the distances from 3.01 to 3.33 Å (Table 3). The HPO₂(OH)[−] anions are connected with each other via hydrogen bonds O(3)–H(2)...O(1) bonds to infinite zigzag chains in the *b* direction (Fig. 1). The HF molecules are attached to the chains through F–H(1)...O(2) hydrogen bonds forming branches directed into the space between the chains.

Table 1
Crystallographic data, some details of data collection and refinement for HF adducts I–III

	CsH ₂ PO ₃ ·HF (I)	KH ₂ PO ₄ ·HF (II)	CsH ₂ PO ₄ ·HF (III)
Formula weight (g mol ^{−1})	233.90	156.09	249.90
Crystal size (mm)	2 × 2 × 0.3	2 × 1.3 × 1	2 × 1.5 × 0.6
Temperature (K)	100	130	30
No. Exp. × Exp.time (h)	6 × 1.7	6 × 1.0	6 × 1.5
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> Å	5.581(2)	6.442(1)	7.840(3)
<i>b</i> Å	4.847(2)	7.557(2)	9.488(4)
<i>c</i> Å	18.333(7)	9.469(2)	14.525(5)
β Å	91.84(3)	101.26(1)	90
<i>V</i> Å ³	495.7(3)	452.1(2)	1080.5(7)
<i>Z</i>	4	4	8
ρ_{calc} (g cm ^{−3})	3.134	2.293	3.073
Reflns total/unique/with <i>I</i> > 2 σ (<i>I</i>)	1332/874/604	2295/1089/793	3503/1200/1187
Refinement reflns. param.	806/83	1074/92	1195/91
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))/w <i>R</i> ₂ (all)	0.067/0.158	0.066/0.163	0.051/0.110

Table 2
Atomic coordinates and equivalent displacement parameters (\AA^2) for I–III

Atom	x/a	y/b	z/c	U_{eq}
CsH₂PO₃·HF (I)				
Cs	0.2789(4)	0.3393(4)	0.0861(1)	0.0141(5)
P	0.7965(4)	−0.2136(5)	0.1744(1)	0.0120(5)
O(1)	1.0605(3)	−0.1526(5)	0.1819(1)	0.0160(5)
O(2)	0.6790(4)	−0.1682(5)	0.0998(1)	0.0184(5)
O(3)	0.7394(4)	−0.5220(5)	0.1953(1)	0.0165(6)
F	0.7811(4)	0.1889(5)	0.0194(1)	0.0192(6)
H(1)	0.7442(6)	0.0340(9)	0.0556(2)	0.0269(9)
H(2)	0.8202(7)	−0.5804(9)	0.2437(2)	0.0259(8)
H(3)	0.6763(7)	−0.0556(10)	0.2263(3)	0.0332(10)
KH₂PO₄·HF (II)				
K	0.1552(4)	0.2265(4)	0.5453(3)	0.0201(6)
P	0.6163(3)	0.2062(3)	0.8306(2)	0.0136(4)
O(1)	0.5908(3)	0.2788(3)	0.6801(2)	0.0158(4)
O(2)	0.7990(2)	0.0787(2)	0.8717(2)	0.0168(4)
O(3)	0.4034(2)	0.1189(3)	0.8519(2)	0.0163(4)
O(4)	0.6416(3)	0.3674(2)	0.9369(2)	0.0172(4)
F	0.0339(3)	0.0265(3)	0.3159(2)	0.0240(5)
H(1)	0.1042(5)	−0.0226(5)	0.2365(3)	0.0278(7)
H(2)	0.3989(6)	−0.0164(5)	0.8406(3)	0.0277(7)
H(3)	0.6308(5)	0.3288(5)	1.0364(3)	0.0270(7)
CsH₂PO₄·HF (III)				
Cs	0.2045(1)	0.5730(1)	0.16482(8)	0.0057(2)
P	0.1921(1)	0.7009(1)	0.43903(8)	0.0051(2)
O(1)	0.2893(1)	0.8371(1)	0.45004(8)	0.0072(2)
O(2)	0.0525(1)	0.7063(1)	0.36766(8)	0.0095(2)
O(3)	0.1150(1)	0.6539(1)	0.53362(8)	0.0073(2)
O(4)	0.3276(1)	0.5844(1)	0.41564(8)	0.0098(2)
F	0.0416(2)	0.8673(1)	0.24293(8)	0.0117(2)
H(1)	0.0500(3)	0.8010(2)	0.2982(2)	0.0192(4)
H(2)	−0.0146(3)	0.6588(2)	0.5395(2)	0.0196(4)
H(3)	0.2833(3)	0.4848(2)	0.4252(2)	0.0197(4)

The structure of KH₂PO₄·HF (II) contains the potassium cation coordinated by 5O and 2F atoms at the distances of 2.64–3.00 Å. The dihydrophosphate anions, PO₂(OH)₂[−], are connected in two mutually orthogonal direction by the hydrogen bonds O(3)–H(2)⋯O(1) and O(4)–H(3)⋯O(1) under formation of layers parallel to the $0yz$ plane (Fig. 2). The HF molecules are held on both sides of the layers by F–H(1)⋯O(2) hydrogen bonds.

In the structure of CsH₂PO₄·HF (III), the Cs cation is surrounded by 6O and 3F atoms at the distances form 3.01 to 3.42 Å. As in structure II, there are two dimensional anions built up from dihydrophosphate anions which are linked by hydrogen bonds O(3)–H(2)⋯O(1) and O(4)–H(3)⋯O(1) (parallel to the $xy0$ plane). The HF molecules are attached by F–H(1)⋯O(2) hydrogen bonds (Fig. 3).

The lengths of P–O bonds are dependent on additional function of O atoms in the hydrogen bonds (Tables 3 and 4). The longest P–O bonds (1.566–

Table 3
Interatomic distances (Å) in structures I–III

	CsH ₂ PO ₃ ·HF (I)	KH ₂ PO ₄ ·HF (II)	CsH ₂ PO ₄ ·HF (III)
P–O(1)	1.504(3)	1.506(2)	1.509(2)
P–O(2)	1.513(3)	1.512(2)	1.509(2)
P–O(3)	1.578(3)	1.570(2)	1.566(2)
P–O(4)	1.408(5) ^a	1.568(3)	1.570(2)
M–O	3.22–3.33	2.78–3.00	3.04–3.42
M–F	3.01–3.22	2.64–2.74	3.01–3.27

^aThe bond P–H(3).

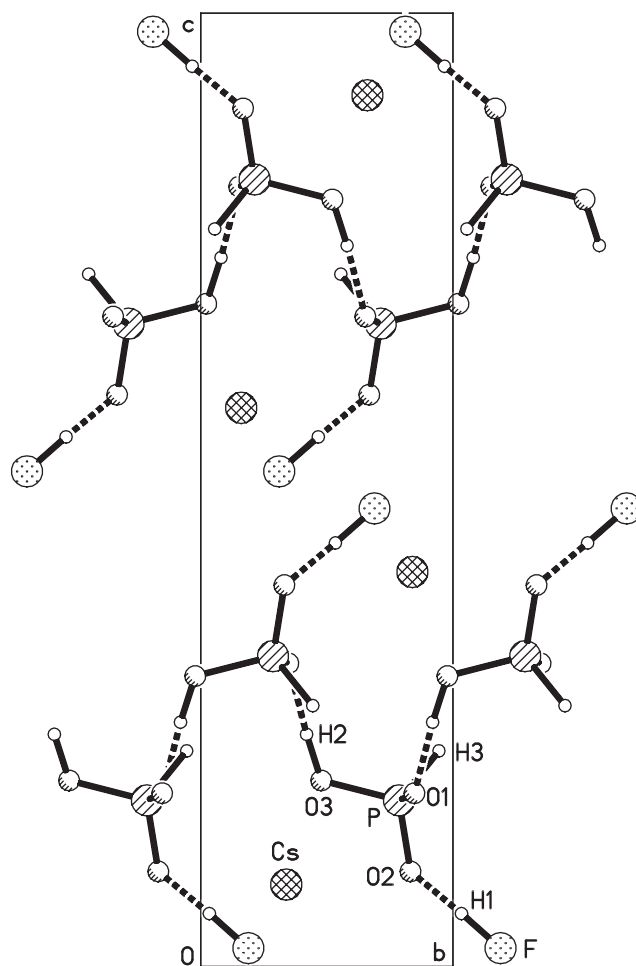


Fig. 1. $0yz$ -Projection of crystal structure of CsH₂PO₃·HF (I). Dashes denote H⋯O hydrogen bonds.

1.578 Å) are for the H-donor function (D), i.e., for P–OH groups. P–O bonds with O atom acting as H-acceptor (A) in hydrogen bonds are significantly shorter, being the shortest for a single H-acceptor function in O–H⋯O bond (1.504 Å for P–O(1) in I), a bit longer for a double H-acceptor function in two such bonds (1.506–1.509 Å for P–O(1) in II and III), and slightly longer for acceptor function in F–H⋯O hydrogen bonds (1.509–1.513 Å for P–O(2) in I–III).

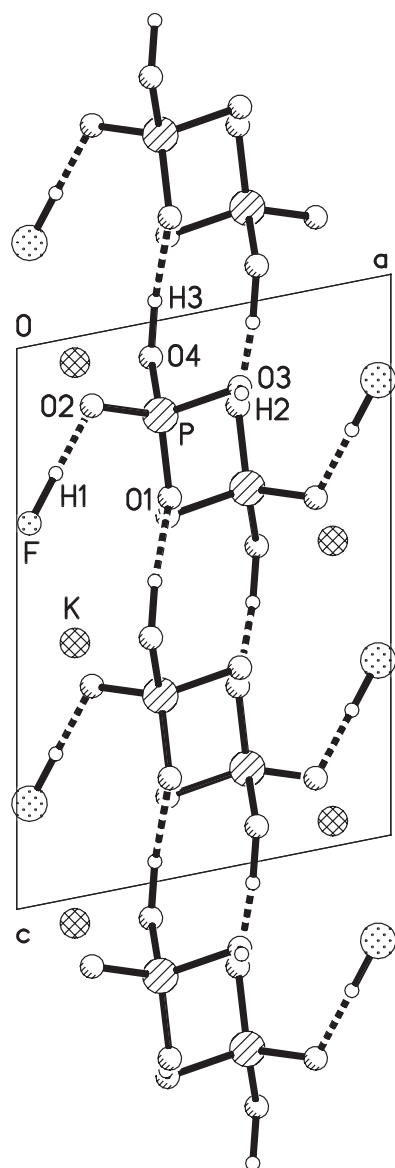


Fig. 2. $x0z$ -Projection of the crystal structure of $\text{KH}_2\text{PO}_4 \cdot \text{HF}$ (**II**). $\text{H} \cdots \text{O}$ hydrogen bonds are shown as dashes.

In structures **I–III**, the $\text{O} \cdots \text{O}$ bonds have the $\text{O} \cdots \text{O}$ ($D-A$) distances in the range 2.56–2.63 Å and, therefore, can be considered as rather strong ones. The longest $\text{O}(4) \cdots \text{H}(3) \cdots \text{O}(1)$ bond in **II**, 2.632(2) Å, is characterized by a smaller angle, 166.2(3)° and a more pronounced asymmetry due to the shortest $\text{O} \cdots \text{H}$ and longest $\text{H} \cdots \text{O}$ distances (Table 4). The $\text{F} \cdots \text{H} \cdots \text{O}$ hydrogen bonds are significantly shorter, 2.356–2.386 Å, with nearly linear arrangement of three atoms, $\angle \text{F} \cdots \text{H} \cdots \text{O}$ 175.3–176.7(4)°. The $\text{F} \cdots \text{H}$ distances in structures **I–III**, 1.020–1.027(5) Å, can be compared with 0.97(2) Å for $\text{F} \cdots \text{D}$ found for crystalline deuterium fluoride by powder neutron diffraction [9]. The difference can be accounted for a weaker interaction $\text{D} \cdots \text{F}$ (resulting in a relatively long $\text{F} \cdots \text{F}$ distance, 2.50(2) Å [9]) as compared with $\text{H} \cdots \text{O}$ in **I–III** due the essentially

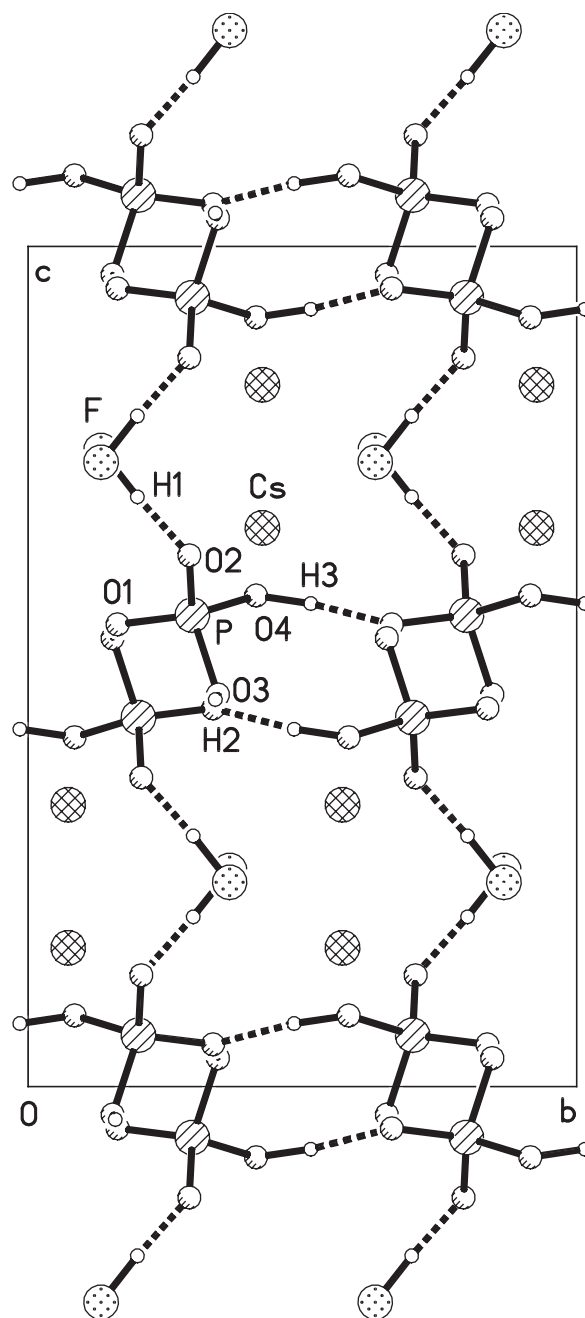


Fig. 3. $0yz$ -Projection of crystal structure of $\text{CsH}_2\text{PO}_4 \cdot \text{HF}$ (**III**). $\text{H} \cdots \text{O}$ hydrogen bonds are shown as dashed lines.

neutral and anionic natures, respectively, of the acceptors. The same $\text{F} \cdots \text{F}$ distance, 2.49(1) Å, was determined for crystalline HF by single-crystal X-ray diffraction [10]. In anionic $(\text{H}_n\text{F}_{n+1})^-$ species, the $\text{F} \cdots \text{F}$ distances are much shorter, being 2.28 Å for symmetrical HF_2^- anions ($n = 1$) [11], 2.33 Å for $n = 2$ [12], 2.40 Å for $n = 3$ [13], and 2.45 Å for $n = 4$ [14].

At present, ten crystal structure have been determined for the HF adducts with acid oxosalts including phosphites [3,5], phosphates [4], sulfates [5,15], and

Table 4
Hydrogen bonds (Å, deg) in structures I–III

Bond, D–H...A	D–H	H...A	D...A	∠ D–H...A
CsH₂PO₃·HF (I)				
F–H(1)...O(2)	1.027(5)	1.330(5)	2.356(3)	175.3(4)
O(3)–H(2)...O(1)	1.022(5)	1.540(5)	2.561(3)	176.9(5)
KH₂PO₄·HF (II)				
F–H(1)...O(2)	1.020(3)	1.367(3)	2.386(2)	176.7(4)
O(3)–H(2)...O(1)	1.028(5)	1.563(4)	2.589(3)	175.5(3)
O(4)–H(3)...O(1)	1.002(3)	1.648(3)	2.632(2)	166.2(3)
CsH₂PO₄·HF (III)				
F–H(1)...O(2)	1.022(3)	1.352(3)	2.371(2)	175.4(2)
O(3)–H(2)...O(1)	1.020(2)	1.546(2)	2.565(2)	178.6(3)
O(4)–H(3)...O(1)	1.017(2)	1.555(3)	2.569(2)	174.1(2)

selenates [5,15]. The whole range of the F...O distances is larger, from 2.35 to 2.45 Å, with the longest one for K₃(SO₄)(HSO₄)·2HF containing two HF molecules hydrogen bonded to the same anion [5]. The condition for stability of such adducts can be formulated as the absence of proton acceptors in the system which are stronger than F[−]. Therefore, only the anions of the acids stronger than HF, such as H₃PO₃, H₃PO₄, H₂SO₄, H₂SeO₄, etc., are able to form HF adducts. On interaction of HF with the salt of weaker acid, proton redistribution should occur under formation of the corresponding acid and F[−] anions. An analogous process takes place in diluted aqueous solutions: HF + H₂O → F[−] + H₃O⁺, thus explaining instability of the HF adducts on dissolving in water. For the same reason, the HF hydrates, (HF)_n(H₂O), should be formulated as hydroxonium fluorides, [H₃O]F (*n* = 1) or hydroxonium hydrofluoride [H₃O][HF₂] (*n* = 2) [2].

The structures of different hydroxonium fluorides and fluorometallates contain normal hydrogen bonds of the type –O–H...F– with an inverse position of hydrogen between F and O atoms. Hydrogen bonds of this type are, as a rule, significantly longer, 2.5–2.7 Å with typical examples in the crystal structures of (H₃O)[TiF₅] (2.51–2.56 Å [16]) or (H₃O)[SbF₆] (2.62–2.71 Å [17]). Similar hydrogen bonds in the crystal structures of (HF)_n(H₂O) are shorter, 2.46–2.47 Å (*n* = 1) and 2.45–2.60 Å (*n* = 2), with the shortest values for the –O–H...F bonds with “isolated” fluoride anion possessing only H-acceptor functions [2].

In conclusion, the formation of the F–H...O hydrogen bonds is possible in the HF adducts with the salts of strong oxoacids. Single-crystal neutron diffraction study of three HF adducts allowed a detailed comparison with the structures of HF and hydrofluorides. The F–H...O bond lengths are intermediate between the values for short O–H...O and F...H...F bonds; F–H...O hydrogen bonds are shorter than typical O–H...F bonds.

Acknowledgments

The authors thank G.J. McIntyre at the ILL for assistance in the collection and treatment of neutron diffraction data.

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