

## On the Geometry of O—H...F Hydrogen Bonds in Metal Fluoride Hydrates

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The geometrical characteristics of O—H...F bonds have been obtained from the analysis of original and literature data on structures of crystal hydrates of metal fluorides. The average O...F distance between the atoms involved in a hydrogen bond is found to be 2.682 Å. All known bonds of this type range from 2.56 to 2.86 Å; this interval is substantially narrower than that for O—H...O bonds. Some other geometrical characteristics of O—H...F hydrogen bonds are also given.

Abundant experimental material on the geometry of hydrogen bonds in crystal hydrates based on the characteristics of O—H...O bonds has been collected and summarized in the reviews of Datt & Ozerov (1972), Ferraris & Franchini-Angela (1972), and Brown (1976). The data on the geometrical parameters of O—H...F bonds are much more limited. Analysis of hydrogen bonds of any type should be based on the results of structural studies of crystals in which the H atoms have been reliably located. Until recently the literature contained only a few examples of structural determinations with location of H atoms of crystal hydrates of metal fluorides having O—H...F bonds (Hamilton, 1962; Abrahams, 1962; Abrahams & Prince, 1962; Luntun & Siew, 1973; Galigné, Durand & Cot, 1974; Prince, 1972). In the last few years the

situation has changed and analysis of the main geometrical parameters of O—H...F bonds in the structures of metal fluoride hydrates has become possible.

The interatomic distances, valence angles and other parameters characterizing the atoms involved in an O—H...F bond fall into two groups. The values that do not depend on the H atom coordinates are referred to as the parameters of the first group. The second group comprises the parameters determined taking into account the positions of the H atoms. Such a division of parameters is most desirable when using the results of structural investigations by X-ray and neutron diffraction methods. The parameters of the first group may be compared and averaged irrespective of the method by which they were obtained. In analysing the parameters

Table 1. *Geometrical parameters of O—H...F bonds in metal fluoride hydrates whose atomic structures were determined from neutron diffraction data*

Compound	Type of bonding X—H...Y	Bond lengths (Å)			XHY	Angles (°)		Distance of H atom from plane Y(1)XY(2) (Å)	References
		X...Y	X—H	H...Y		H(1)XH(2)	Y(1)XY(2)		
FeSiF <sub>6</sub> ·6H <sub>2</sub> O	O—H(1)...F(1)	2.68	0.86	1.85	161.0	111.9	133.4	—	Hamilton (1962)
	O—H(2)...F(2)	2.72	0.92	1.82	168.0	—	—	—	
CuF <sub>2</sub> ·2H <sub>2</sub> O (T = 4.2 K)	O—H...F	2.660	0.959	1.707	167.7	110.1	96.4	—	Abrahams (1962)
CuF <sub>2</sub> ·2H <sub>2</sub> O (T = 298 K)	O—H...F	2.717	0.965	1.692	167.6	110.6	96.5	—	Abrahams & Prince (1962), Prince (1972)
ZnF <sub>2</sub> ·4H <sub>2</sub> O	O(1)—H(1)...F(2)	2.56	0.95	1.62	175.3	—	—	0.05	Bukvetsky, Nozik & Simonov (1976b)
	O(1)—H(8)...F(1)	2.61	0.96	1.68	160.3	109.1	106.9	0.20	
	O(2)—H(5)...F(1)	2.67	0.93	1.74	173.0	—	—	−0.07	
	O(2)—H(6)...O(4)	—	—	—	—	109.0	108.1	0.02	
	O(3)—H(3)...F(2)	2.72	0.98	1.75	168.5	—	—	0.12	
	O(3)—H(4)...O(1)	—	—	—	—	111.4	112.9	0.04	
	O(4)—H(2)...F(2)	2.62	0.99	1.66	164.5	—	—	−0.13	
	O(4)—H(7)...F(1)	2.61	1.00	1.62	174.8	106.4	96.8	0.01	

Table 2. Geometrical parameters of O—H...F bonds in metal fluoride hydrates whose atomic structures were determined from X-ray diffraction data

Compound	Type of bonding X—H...Y	Bond lengths (Å)				Angles (°)		Distance of H atom from plane Y(1)XY(2) (Å)	References
		X...Y	X—H	H...Y	XHY	H(1)XH(2)	Y(1)XY(2)		
SrTiF <sub>6</sub> ·2H <sub>2</sub> O ( <i>t</i> = -100°C)	O(1)—H(1)	—	—	—	—	94.7	—	—	Bukvetsky, Davidovich & Simonov (1975)
	O(1)—H(2)...F	2.75	0.97	1.82	164.6	—	—	—	
	O(2)—H(1)...O	—	—	—	—	106.9	—	—	
	O(2)—H(2)...F	2.77	0.89	2.00	143.7	—	—	0.01	
ZnF <sub>2</sub> ·4H <sub>2</sub> O	O(1)—H(1)...F(2)	2.57	0.91	1.66	172.7	102.2	106.7	-0.07	Bukvetsky <i>et al.</i> (1973)
	O(1)—H(8)...F(1)	2.63	0.71	1.93	168.6	—	—	-0.09	
	O(2)—H(5)...F(1)	2.68	0.63	2.07	160.8	108.8	108.1	0.12	
	O(2)—H(6)...O(4)	—	—	—	—	—	—	-0.10	
	O(3)—H(3)...F(2)	2.70	0.94	1.81	157.6	—	—	0.02	
	O(3)—H(4)...O(1)	—	—	—	—	111.5	112.8	0.13	
	O(4)—H(2)...F(2)	2.62	0.69	1.95	164.9	—	—	0.00	
	O(4)—H(7)...F(1)	2.62	0.77	1.85	174.1	111.7	96.5	0.01	
ZnInF <sub>5</sub> ·7H <sub>2</sub> O	O(1)—H(3)...F(5)	2.73	0.81	1.92	170.0	—	—	-0.10	Bukvetsky, Polishchuk & Simonov (1977)
	O(1)—H(4)...O(4)	—	—	—	—	98.6	—	0.03	
	O(2)—H(9)...F(5)	2.72	0.78	1.95	171.8	—	—	0.06	
	O(2)—H(10)...F(2)	2.69	0.88	1.81	172.9	108.2	112.9	0.07	
	O(3)—H(11)...F(4)	2.62	0.88	1.74	176.1	—	—	0.03	
	O(3)—H(12)...F(1)	2.65	0.78	1.87	174.6	105.8	111.2	-0.01	
	O(4)—H(5)...F(4)	2.67	0.92	1.75	173.1	—	—	0.05	
	O(4)—H(6)...F(3)	2.63	0.77	1.86	173.2	106.7	113.9	0.04	
	O(5)—H(1)...F(1)	2.69	0.80	1.90	173.4	—	—	-0.06	
	O(5)—H(2)...F(2)	2.73	0.78	1.95	176.1	107.6	104.4	-0.01	
	O(6)—H(7)...F(2)	2.72	0.79	1.94	165.7	—	—	0.01	
	O(6)—H(8)...F(3)	2.63	0.89	1.74	174.0	104.6	90.6	-0.02	
	O(7)—H(13)...F(5)	2.68	0.85	1.84	167.3	—	—	0.06	
	O(7)—H(14)...O(3)	—	—	—	—	103.0	97.0	0.02	
CdGaF <sub>5</sub> ·7H <sub>2</sub> O	O(1)—H(1)...F(5)	2.69	0.88	1.81	173.6	—	—	-0.03	Bukvetsky <i>et al.</i> (1977)
	O(1)—H(2)...F(4)	2.69	0.82	1.87	175.2	110.8	115.3	0.05	
	O(2)—H(3)...F(2)	2.70	0.90	1.80	171.1	—	—	0.01	
	O(2)—H(4)...F(1)*	3.10	—	—	—	109.4	—	—	
	O(2)—H(4)...F(2)	2.84	0.70	2.39	123.4	—	108.0	0.40	
	O(3)—H(5)...F(1)	2.65	0.79	1.86	175.5	—	—	-0.04	
	O(3)—H(6)...F(3)	2.63	0.79	1.84	172.3	106.3	102.6	0.06	
	O(4)—H(7)...O(1)	—	—	—	—	—	—	0.03	
	O(4)—H(8)...F(2)	2.63	0.83	1.81	170.1	100.0	102.8	0.02	
	O(5)—H(9)...O(7)	—	—	—	—	—	—	-0.01	
	O(5)—H(10)...F(4)	2.86	0.84	2.03	168.3	102.7	110.7	0.11	
	O(6)—H(11)...F(1)	2.67	0.95	1.71	179.0	—	—	-0.005	
	O(6)—H(12)...F(5)	2.68	0.77	1.92	168.8	108.0	107.6	0.11	
	O(7)—H(13)...F(4)	2.65	0.85	1.81	168.7	—	—	0.09	
O(7)—H(14)...F(3)	2.71	0.72	2.00	171.6	102.2	112.3	0.05		
RbVF <sub>4</sub> ·2H <sub>2</sub> O	O(1)—H(1)...F(1)	2.56	0.93	1.61	178.0	—	—	0.01	Bukvetsky <i>et al.</i> (1976a)
	O(1)—H(2)...F(2)	2.57	0.91	1.63	177.0	110.0	114.1	-0.02	
CoSiF <sub>6</sub> ·6H <sub>2</sub> O	O(1)—H(1)...F(1)	2.785	—	—	—	—	—	—	Lunton & Siew (1973)
	O(1)—H(2)...F(2)	2.711	—	—	—	—	—	—	
LiKPO <sub>3</sub> F·H <sub>2</sub> O	O(1)—H(1)...F*	3.183	—	—	—	—	—	—	Galigné <i>et al.</i> (1974)
	O(1)—H(2)...O	—	—	—	—	—	—	—	

\* In the statistical treatment this bond was not taken into account.

of the second group, one should take into consideration the strong polarization of H atoms engaged in hydrogen bonds and deviations in the coordinates of the nucleus and centre of gravity of the electron cloud of such atoms determined by the neutron and X-ray methods respectively. For this reason, the geometries of the O—H...F bonds obtained from neutron diffraction and X-ray structural determinations are summarized in two different tables. Table 1 contains the parameters of ten crystallographically independent O—H...F bonds found in four metal fluoride hydrates whose structures were solved and refined from neutron diffraction data. The similar characteristics for 38 crystallographically independent O—H...F bonds in seven metal fluoride hydrates investigated by X-ray structure analysis are given in Table 2.

Of the characteristics independent of the positions of the H atoms the distance between the O and F atoms involved in a hydrogen bond is most interesting. For the 42 H bonds for which data are available to us, the average length is 2.704 Å ( $\sigma = 0.115$  Å), if its minimum and maximum values are, respectively, 2.56 Å [RbVF<sub>4</sub>·2H<sub>2</sub>O (Bukvetsky, Muradyan, Davidovich & Simonov, 1976a), ZnF<sub>2</sub>·4H<sub>2</sub>O (Bukvetsky, Polishchuk & Simonov, 1973)] and 3.18 Å [LiKPO<sub>3</sub>F·H<sub>2</sub>O (Galigné *et al.*, 1974)]. Analysis of the histogram (Fig. 1) shows that we can omit from consideration two 'bonds' with O...F distances of 3.10 and 3.18 Å. The remaining 40 O...F distances between the atoms involved in a hydrogen bond are

then seen to be distributed according to the normal rule with a mean value of 2.682 Å and dispersion,  $\sigma^2$ , of 0.00431 Å<sup>2</sup> ( $\sigma = 0.066$  Å). This mean value of the O...F distance is significantly smaller than that found for the O...O distance in O—H...O bonds which, according to Ferraris & Franchini-Angela (1972), is 2.810 Å. The second peculiarity of the O—H...F hydrogen bonds (compared with O—H...O bonds) is the dispersion of the distribution of the O...F distances being less than approximately three times the value of the corresponding dispersion of the distribution of the O...O distances in O—H...O bonds. The dispersion in the O...O case is  $\sigma^2 = 0.0121$  Å<sup>2</sup> ( $\sigma = 0.11$  Å) (Ferraris & Franchini-Angela, 1972). All the 40 O—H...F bonds tend to be distributed within a rather narrow range of distances from 2.56 to 2.86 Å.

The values of the angles between the bonds of the donor O atoms of the water molecule to two acceptor H bonds fluctuate between 90.6 and 115.3° with a mean value of 106.1°.

The next feature of the hydrogen bond is that the O—H distance depends considerably on the position of the H atom. If we reject the shortest and longest O—H bonds and average the remaining ones, the mean value of the O—H distance for O—H...F bonds determined from eight independent neutron diffraction measurements is 0.957 Å ( $\sigma = 0.029$  Å). This coincides within experimental error with the average donor O—H bond in the O—H...O bonds deduced from neutron diffraction studies. The mean value of the O—H distance in

Table 3. Geometrical parameters of bonds of the type  $\text{O} \begin{cases} \text{H}(1)\cdots\text{F} \\ \text{H}(2)\cdots\text{O}(1) \end{cases}$  in metal fluoride hydrates

Compound (radiation)	Type of bonding	Distances (Å)				Angles (°)			References
		O...F O(1)	$\text{O} \begin{cases} \text{H}(1) \\ \text{H}(2) \end{cases}$	H(1)...F H(2)...O(1)	OH(1)F OH(2)O(1)	H(1)OH(2)	FOO(1)		
ZnF <sub>2</sub> ·4H <sub>2</sub> O (neutrons)	O(2) $\begin{cases} \text{H}(5)\cdots\text{F}(1) \\ \text{H}(6)\cdots\text{O}(4) \end{cases}$	2.67	0.93	1.74	173.0	109.0	108.1	Bukvetsky <i>et al.</i> (1976b)	
		2.92	0.99	1.93	177.8				
	O(3) $\begin{cases} \text{H}(3)\cdots\text{F}(2) \\ \text{H}(4)\cdots\text{O}(1) \end{cases}$	2.72	0.98	1.75	168.5	111.4	112.9		
		2.81	0.91	1.90	176.1				
ZnF <sub>2</sub> ·4H <sub>2</sub> O (X-rays)	O(2) $\begin{cases} \text{H}(5)\cdots\text{F}(1) \\ \text{H}(6)\cdots\text{O}(4) \end{cases}$	2.68	0.63	2.07	160.8	108.8	108.1	Bukvetsky <i>et al.</i> (1973)	
		2.92	1.02	1.92	162.7				
	O(3) $\begin{cases} \text{H}(3)\cdots\text{F}(2) \\ \text{H}(4)\cdots\text{O}(4) \end{cases}$	2.70	0.94	1.81	157.6	111.5	112.8		
		2.82	0.82	2.05	157.0				
SrTiF <sub>6</sub> ·2H <sub>2</sub> O ( <i>t</i> = -100°C) (X-rays)	O(2) $\begin{cases} \text{H}(3)\cdots\text{F}(5) \\ \text{H}(4)\cdots\text{O}(1) \end{cases}$	2.77	0.89	2.00	143.8	106.9	125.2	Bukvetsky <i>et al.</i> (1975)	
		2.94	0.83	2.18	152.7				
ZnInF <sub>5</sub> ·7H <sub>2</sub> O (X-rays)	O(1) $\begin{cases} \text{H}(3)\cdots\text{F}(5) \\ \text{H}(4)\cdots\text{O}(4) \end{cases}$	2.73	0.81	1.92	170.0	98.6	93.1	Bukvetsky <i>et al.</i> (1977)	
		2.77	0.67	2.10	174.5				
	O(7) $\begin{cases} \text{H}(13)\cdots\text{F}(5) \\ \text{H}(14)\cdots\text{O}(3) \end{cases}$	2.68	0.85	1.84	167.3	103.0	97.0		
		2.73	0.74	1.99	176.8				
CdGaF <sub>5</sub> ·7H <sub>2</sub> O (X-rays)	O(4) $\begin{cases} \text{H}(8)\cdots\text{F}(2) \\ \text{H}(7)\cdots\text{O}(1) \end{cases}$	2.63	0.83	1.81	170.1	100.0	102.8	Bukvetsky <i>et al.</i> (1977)	
		2.81	0.83	2.00	166.1				
	O(5) $\begin{cases} \text{H}(10)\cdots\text{F}(4) \\ \text{H}(9)\cdots\text{O}(7) \end{cases}$	2.86	0.84	2.03	168.1	102.7	110.7		
		2.86	0.89	1.97	172.7				

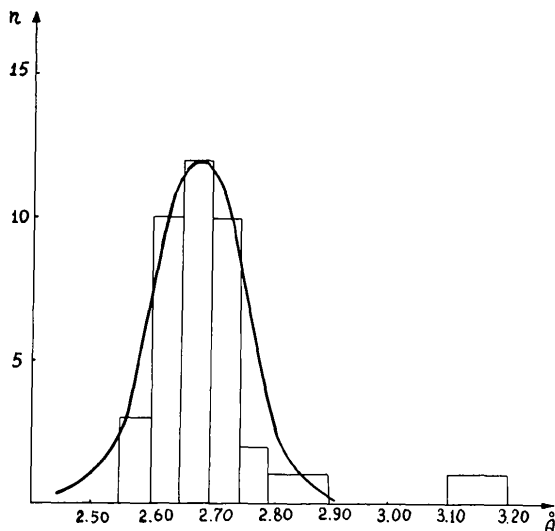


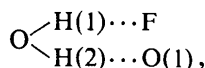
Fig. 1. A histogram showing the O—H...F hydrogen-bond lengths.

O...F bonds in metal fluoride hydrates from X-ray structure analyses is  $0.827 \text{ \AA}$  ( $\sigma = 0.081 \text{ \AA}$ ). It thus follows that the systematic displacement between the positions of the nuclei and centres of gravity of the electron cloud of the water molecule H atoms, due to polarization of these, reaches  $0.13 \text{ \AA}$ .

The average length of the acceptor H...F bond determined from 10 neutron diffraction measurements is  $1.714 \text{ \AA}$  ( $\sigma = 0.073 \text{ \AA}$ ) while for 33 bonds (excluding a bifurcated hydrogen bond) derived from X-ray data it is  $1.850 \text{ \AA}$  ( $\sigma = 0.109 \text{ \AA}$ ). For the O—H...O bonds the analogous value determined from neutron diffraction data is  $1.876 \text{ \AA}$ .

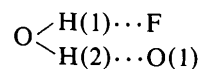
Studies of bent O—H...F bonds, *i.e.* of the OHF angles, show that their mean value obtained from neutron diffraction data is  $169.7^\circ$  and that the scatter of these angles is characterized by  $\sigma = 5.6^\circ$ . This mean value agrees well with that found for the O—H...O bond (Brown, 1976). The average OHF angle taken from X-ray structural results is  $172.3^\circ$  ( $\sigma = 3.0^\circ$ ).

Seven crystallographically independent molecules of water whose H atoms take part in bonds of different types,



have been revealed in investigated structures of metal fluoride hydrates (Table 3). The geometrical characteristics of these bonds are as follows. The lengths of

the O...F and O...O(1) bonds lie in the ranges  $2.63\text{--}2.83 \text{ \AA}$  and  $2.73\text{--}2.94 \text{ \AA}$  respectively. The average O—H(1) and O—H(2) distances obtained from X-ray data are found to coincide, at  $0.83 \text{ \AA}$ . In this case the average H(1)...F and H(2)...O bonds are different, being equal to  $1.97$  and  $2.03 \text{ \AA}$  respectively. In other words, when the same molecule of water is involved in two different hydrogen bonds, the O—H(1)...F bonds appear to be shorter than the O—H(2)...O(1) bonds. Here the O—H(1)...F bonds are bent more sharply than the O—H(2)...O(1) bonds, the average angles OH(1)F and OH(2)O(1) being  $162.6^\circ$  and  $166.1^\circ$  respectively. Neutron diffraction studies of the structure of  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$  indicate the similar relationships between the geometrical parameters of the O—H(1)...F and O—H(2)...O(1) bonds; the O...F and O...O(1) distances are, respectively,  $2.70$  and  $2.86 \text{ \AA}$ . The OH(1)F and OH(2)O(1) angles are  $170.8^\circ$  and  $177.0^\circ$  respectively. Thus the parameters of the



bonds confirm the conclusion that the O—H...F bonds, as compared with the O—H...O bonds, are, on average, shorter and are characterized by a smaller scatter of lengths and a sharper bending.

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