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The crystal structure of a new form of the dipotassium pentafluoroaluminate hydrate, $K_2AlF_5 \cdot H_2O$, and of its dehydrate, K_2AlF_5

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Abstract

A new form of $K_2AlF_5 \cdot H_2O$ has been prepared under hydrothermal conditions, i.e., 650 °C, 1800 bar. It is monoclinic: $a = 6.133(3)$ Å, $b = 7.475(4)$ Å, $c = 6.142(3)$ Å, $\beta = 97.17(2)°$, $\rho = 2.59$ g cm^{-3}, $Z = 2$, space group $P2_1/m$. The crystal structure has been determined using 737 independent single-crystal X-ray reflections ($R = 0.030$, $R_w = 0.028$) and is isotypic with the low-temperature form of $K_2MnF_5 \cdot H_2O$. It is characterized by slightly kinked endless chains of aluminium octahedra sharing opposite corners and running along the [010] direction. The water molecule is not coordinated to the aluminium atom, but is linked by two hydrogen bonds, O–H···F, to two successive $[AlF_6]$ octahedra of the same chain. The potassium atoms are 12-coordinated by 10 fluorine atoms and two water molecules. $K_2AlF_5 \cdot H_2O$ can be easily and reversibly dehydrated at 80–100 °C to tetragonal K_2AlF_5: $a = 5.965(1)$ Å, $c = 3.699(1)$ Å, $Z = 1$, space group $P4/mmm$. Its crystal structure is deduced from that of the monohydrated form and both are described with the same framework.

Keywords: Potassium aluminium fluoride; $K_2AlF_5 \cdot H_2O$; K_2AlF_5; Crystal structure; X-ray powder pattern

1. Introduction

Hydrated fluorides with the chemical formula $K_2M^{III}F_5 \cdot H_2O$ (M^{III} = Al [1,2], Mn [3,4], Fe [5]) have been reported. The aluminium compound is orthorhombic: space group *Cmcm*; the manganese (at room temperature) and the iron compounds are monoclinic, but with two different space groups: $P2_1/m$ and $C2/c$. The structures of the two first fluorides contain infinite chains of fluoro-bridged octahedra $[MF_5]_n^{2n-}$, whereas in the iron compound isolated $[FeF_5(H_2O)]^{2-}$ ions are apparent. $K_2MnF_5 \cdot H_2O$ undergoes a second-order phase transition at 81 °C [4] from a monoclinic ($P2_1/m$) to an orthorhombic (*Cmcm*) symmetry. All other hydrated fluorides with an analogous chemical formula: $A^I_2M^{III}F_5 \cdot H_2O$ (A^I = Rb, M^{III} = Al [6]; A^I = Tl, M^{III} = Al [6,7]; A^I = Rb, M^{III} = Mn [4,8]; A^I = Tl, M^{III} = Mn [9]; A^I = Rb, M^{III} = Fe [6]) are orthorhombic, space group *Cmcm*, isostructural with o-$K_2AlF_5 \cdot H_2O$.

2. Experimental details

2.1. Synthesis of monoclinic m-$K_2AlF_5 \cdot H_2O$

This new form of $K_2AlF_5 \cdot H_2O$ was prepared under hydrothermal synthesis conditions. A steel bomb containing a sealed gold tube, into which was introduced a stoichiometric mixture of KF and AlF_3 in 40% aqueous hydrofluoric acid solution, was heated up to 650 °C under 1800 bar pressure. After heating for 2 d, the bomb was cooled and the tube opened. It contained a large number of colourless parallelepipedic single crystals. Most of these were twinned with a common *b* axis. Nevertheless their crystal symmetry and cell parameters could be determined using classical X-ray diffraction methods. The cell is monoclinic: $a = 6.133(3)$ Å, $b = 7.475(4)$ Å, $c = 6.142(3)$ Å, $\beta = 97.17(2)°$, $Z = 2$. Only one reflection condition was observed: $0k0$, $k = 2n$, leading to two possible space groups: $P2_1$ and $P2_1/m$. The two cell parameters *a* and *c* are very close, but unambiguously different as observed on the Weissenberg and Buerger photographs of several single crystals.

A portion of the crystals prepared was powdered and the X-ray diffraction pattern recorded: this is given in Table 1.

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Table 1
d-Spacings (Å) in m-$K_2AlF_5 \cdot H_2O$

$d_{exp.}$	$d_{calc.}$	$h\ k\ l$	I/I_o	$d_{exp.}$	$d_{calc.}$	$h\ k\ l$	I/I_o
6.09	6.094	0 0 1	64	1.959	1.959	2 1 2	18
	6.085	1 0 0					
4.718	4.723	0 1 1	5	1.926	1.929	0 3 2	4
	4.719	1 1 0			1.928	2 3 0	
3.568	3.568	1 1 1	12	1.881	1.882	1 3 $\bar{2}$	7
					1.881	2 3 $\bar{1}$	
3.187	3.186	0 2 1	33	1.869	1.869	0 4 0	56
	3.185	1 2 0					
3.043	3.047	0 0 2	22	1.803	1.804	1 1 3	4
	3.043	2 0 0			1.802	3 1 1	
2.902	2.901	1 2 $\bar{1}$	51	1.787	1.787	0 4 1	5
					1.786	1 4 0	
2.819	2.822	0 1 2	17	1.745	1.746	2 1 $\bar{3}$	8
	2.818	2 1 0			1.745	3 1 $\bar{2}$	
2.751	2.750	1 2 1	38	1.619	1.619	2 2 $\bar{3}$	10
					1.618	3 2 $\bar{2}$	
2.679	2.681	1 1 $\bar{2}$	23	1.592	1.593	0 4 2	6
	2.679	2 1 $\bar{1}$			1.592	2 4 0	
2.594	2.598	1 0 2	5	1.574	1.574	2 3 2	8
	2.596	2 0 1					
2.449	2.454	1 1 2	4	1.534	1.534	3 0 $\bar{3}$	6
	2.452	2 1 1					
2.361	2.362	0 2 2	100	1.523	1.524	0 0 4	7
	2.360	2 2 0			1.521	4 0 0	
2.302	2.301	2 0 $\bar{2}$	62	1.492	1.493	1 1 $\bar{4}$	5
					1.491	4 1 $\bar{1}$	
2.030	2.030	2 0 2	45	1.451	1.451	2 4 $\bar{2}$	21

Because of orientation problems due to the single-crystal origin of the powder, the reported intensities are those calculated after structure refinement. Splitting of the *hkl* lines, which must occur when $h \neq l$ for the same k value, was not observed.

Table 2
Crystal data, data collection and refinement characteristics

Symmetry: monoclinic; space group: $P2_1/m$ (11)
Refined cell parameters:
$a = 6.133(3)$ Å, $b = 7.475(4)$ Å, $c = 6.142(3)$ Å, $\beta = 97.17(2)°$,
$V = 279.4(4)$ Å^3, $Z = 2$, $M = 218.19$ g mol^{-1}.
Density: 2.59 g cm^{-3} (calculated)
Crystal size: $0.08 \times 0.11 \times 0.11$ mm^3
Radiation: Mo Kα ($\lambda = 0.71069$ Å)
Linear absorption coefficient: 18.64 cm^{-1}
No absorption correction made
36 steps per reflection, 4 s max. per step
Intensity measurements up to $2\theta = 70°$
Indices: $-9 \leqslant h \leqslant 9$; $0 \leqslant k \leqslant 12$; $0 \leqslant l \leqslant 9$
1792 measured reflections; 1125 independent reflections: $R_{int} = 0.0136$
737 independent reflections with $F/\sigma(F) > 4$
53 refined parameters
Weighting scheme: $w = 1.1976/(\sigma^2(F) + 2.27 \times 10^{-4} F^2)$
Secondary extinction factor: 25.7×10^{-8}
Reliability factors: $R = 0.030$; $R_w = 0.028$
Electron density in Fourier difference map:
maximum height: 0.45 e Å^{-3}; minimum height: -0.50 e Å^{-3}

2.2. Structural determination of m-$K_2AlF_5 \cdot H_2O$

One single crystal was selected from among the many twinned species. Intensity data were collected on a Siemens Stoe AED 2 four-circle diffractometer. Corrections were applied for Lorentz and polarization effects. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography* [10]. The experimental conditions are listed in Table 2. All the refinement calculations were performed on an IBM RISC 6000 computer using the SHELX-76 program [11]. A list of the structure factors may be obtained from the authors on request.

The structural determination started in the centrosymmetric space group $P2_1/m$ with the hypothesis that the aluminium atom was located on the origin of the cell, as in the orthorhombic form. Thus, having placed the aluminium atom in the special position 2a, a first Fourier synthesis gave the positions of the potassium atoms in two distinct sites 2e. A new Fourier synthesis immediately gave the positions of three fluorine and one oxygen atoms. Refinement of their atomic coordinates caused the reliability factor to drop to $R = 0.089$. With anisotropic thermal motion, R became 0.034. At this stage of the structure determination and in order to localize the hydrogen atoms of the water molecule, a final difference Fourier map was established. It clearly gave the general posi-

Table 3
Atomic coordinates and parameters of anisotropic thermal motion ($\times 10^4$) (with esds in parentheses) for m-$K_2AlF_5 \cdot H_2O$

Atom/site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
K(1)/(2e)	0732(1)	$\frac{1}{4}$	5011(1)	331(3)	210(3)	220(3)	0	11(3)	0	2.02
K(2)/(2e)	5013(1)	$\frac{1}{4}$	0734(1)	211(3)	212(3)	339(4)	0	12(3)	0	2.02
Al(1)/(2a)	0	0	0	124(3)	83(3)	134(3)	3(3)	−7(2)	6(3)	0.91
F(1)/(2e)	0013(3)	$\frac{1}{4}$	0019(3)	328(8)	82(7)	346(8)	0	−14(7)	0	2.03
F(2)/(4f)	8079(2)	9999(2)	1925(2)	367(6)	254(7)	375(6)	103(6)	206(5)	109(6)	2.51
F(3)/(4f)	2191(2)	9998(2)	2190(2)	340(6)	214(6)	330(6)	10(7)	−181(5)	8(7)	2.48
O(1)/(2e)	5358(4)	$\frac{1}{4}$	5358(4)	336(11)	234(10)	377(11)	0	−86(9)	0	2.58
H(1)/(4f)	4077(15)	6682(15)	4101(15)	250 *	–	–	–	–	–	1.97 [a]

[a] B_{eq} fixed to 1.97 Å^2.

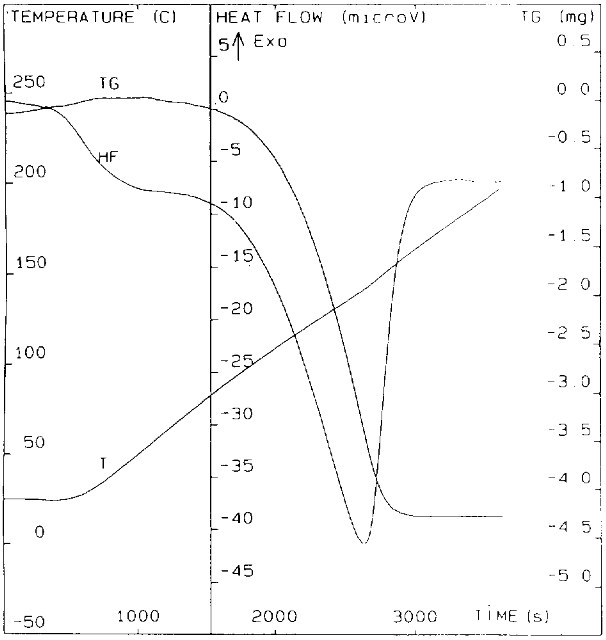

Fig. 1. Thermogravimetric/differential thermal analyses curves of $K_2AlF_5 \cdot H_2O$.

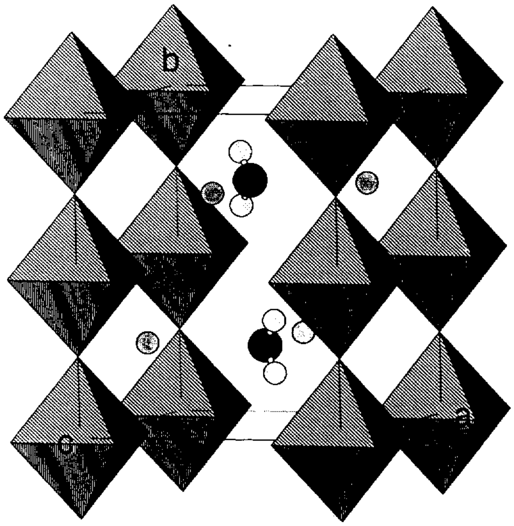

Fig. 2. Perspective view of the structure of m-$K_2AlF_5 \cdot H_2O$.

tion 4f of these atoms. The R factor yielded a value of 0.030 ($R_w = 0.028$).

Calculations performed in the non-centrosymmetric space group $P2_1$ did not significantly improve the previous results. Table 3 gives the final set of atomic parameters.

2.3. Dehydration of $K_2AlF_5 \cdot H_2O$

$K_2AlF_5 \cdot H_2O$ is readily dehydrated at low temperature as shown by the thermogravimetric/differential thermal analyses curves depicted in Fig. 1. Dehydration commenced at 60 °C and was complete at 140 °C (heating rate: 180 °C h^{-1}). Anhydrous K_2AlF_5 is not stable at room temperature and rehydrates spontaneously to its monohydrate after a few days.

3. Results

3.1. The structure of $K_2AlF_5 \cdot H_2O$

The global structure is represented in Figs. 2 and 3 and is quite similar to that of the orthorhombic form [1,2]. It is built up from infinite very slightly kinked chains, running

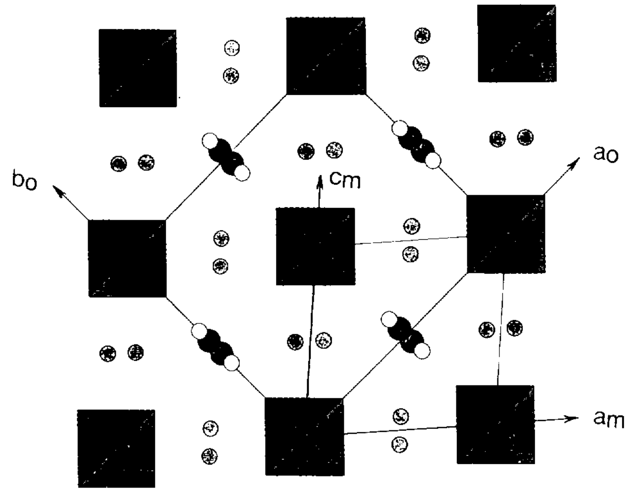

Fig. 3. The [010] projection of the structure of m-$K_2AlF_5 \cdot H_2O$. Comparison with the [001] projection of the structure of o-$K_2AlF_5 \cdot H_2O$.

Table 4
Interatomic distances (Å) and bond angles (°) for the [AlF_6] octahedra in *m*-$K_2AlF_5 \cdot H_2O$

Al	F(2)	F(2)	F(3)	F(3)	F(1)	F(1)
F(2)	**1.770**	3.540	2.507	2.512	2.573	2.575
F(2)	180.0	**1.770**	2.512	2.507	2.575	2.573
F(3)	89.9	90.1	**1.779**	3.557	2.572	2.588
F(3)	90.1	89.9	180.0	**1.779**	2.588	2.572
F(1)	89.9	90.1	89.6	90.4	**1.869**	3.738
F(1)	90.1	89.9	90.4	89.6	180.0	**1.869**

Average ⟨Al–F⟩ = 1.806 Å.

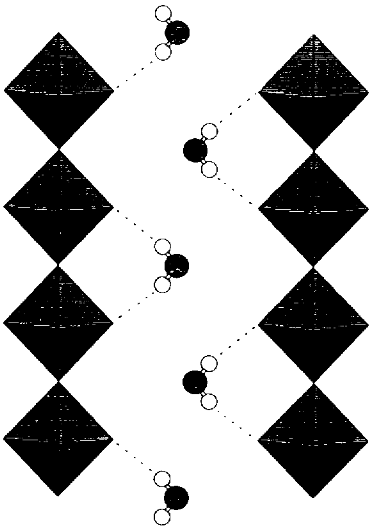

Fig. 4. Perspective view of the ($\bar{1}$01) plane showing linkage of the water molecules via hydrogen bonds to two fluorine atoms of the same $[AlF_5]_n^{2n-}$ infinite chain.

Table 5
Water molecules and hydrogen bonding in *m*-$K_2AlF_5 \cdot H_2O$: interatomic distances (Å) and bond angles (°); comparison with the orthorhombic form in parentheses [2]

O–H	0.759 (0.855)	H···F	1.988 (1.897)
H–H	1.223 (1.399)	O···F	2.729 (2.726)
H–O–H	107.4 (109.8)	O–H···F	165.4 (163.1)

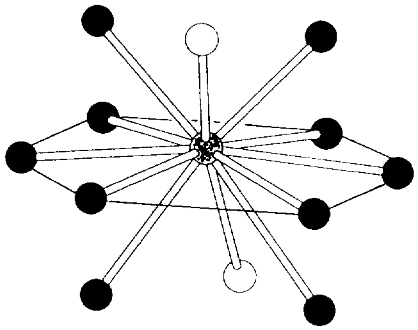

Fig. 5. The [$\bar{1}$10] projection of the coordination polyhedron of K^+. The dark circles depict the fluorine atoms and open circles the oxygen atoms of the water molecules.

Table 6
Interatomic K–F and K–OH_2 distances (Å) in the 12-fold potassium coordination polyhedra of *m*-$K_2AlF_5 \cdot H_2O$

K(1)		K(2)	
2×2.687	F(2)	2×2.687	F(2)
2×2.773	F(3)	2×2.771	F(3)
2.818	OH_2	2.821	OH_2
2×2.994	F(2)	2×2.997	F(2)
3.043	F(1)	3.043	F(1)
3.161	F(1)	3.152	F(1)
2×3.229	F(3)	2×3.228	F(3)
3.329	OH_2	3.335	OH_2
Mean K–F distance: 2.957 Å		Mean K–F distance: 2.956 Å	

along the *b* axis, of distorted [AlF_6] octahedra sharing opposite corners. Table 4 gathers together the interatomic distances and bond angles in the octahedra, showing four short [terminal fluorine atoms F(2) and F(3)] and two long Al–F distances [bridging fluorine atom F(1)]. The tilting of the octahedra along the screw axis 2_1 is very small, with an Al–F(1)–Al angle of 179.2°, almost equal to that observed in the orthorhombic form (179.4°) [2].

The oxygen atoms of the water molecules lie in the mirror planes at $y = 1/4$ and $y = 3/4$. These water molecules are weakly linked by two hydrogen bonds O–H···F(3) to two successive [AlF_6] octahedra in the same chain as shown in Fig. 4. Table 5 gathers together the characteristic interatomic distances and bond angles. The O–H distances (0.759 Å) are shorter here than in the orthorhombic form (0.855 Å), but are of the same order as observed in $MnFeF_5 \cdot 2H_2O$ [12] or $Pb_{1.5}Fe_3F_{12} \cdot 3H_2O$ [13]: 0.74 Å. This is the main difference between the two forms of $K_2AlF_5 \cdot H_2O$, probably due to the different local symmetries of the anions: O atoms lie in site 4c (symmetry: *m*2*m*) in the orthorhombic form and in site 2e (symmetry: *m*) in the monoclinic one.

The potassium atoms are 12-coordinated by 10 fluorine atoms and two water molecules, as shown in Fig. 5 and Table 6. The water molecules complete a distorted cubic close-packed arrangement of potassium and fluorine atoms; hence, the structure can also be described as a cubic close-packed arrangement of potassium, oxygen and fluorine atoms, with aluminium atoms in the fluorine octahedral holes.

3.2. The structure of anhydrous K_2AlF_5

The X-ray powder pattern of K_2AlF_5 is given in Table 7. It can be indexed on the basis of a tetragonal cell:

Table 7
d-Spacings (Å) in K_2AlF_5

$d_{exp.}$	$d_{calc.}$	*h k l*	I/I_o	$d_{exp.}$	$d_{calc.}$	*h k l*	I/I_o
5.969	5.965	1 0 0	100	2.108	2.109	2 2 0	17
4.222	4.218	1 1 0	7	1.886	1.886	3 1 0	3
3.145	3.144	1 0 1	7	1.849	1.849	0 0 2	8
2.983	2.983	2 0 0	21	1.767	1.767	1 0 2	3
2.781	2.781	1 1 1	20	1.681	1.681	3 1 1	4
2.669	2.668	2 1 0	6	1.655	1.655	3 2 0	3
2.322	2.322	2 0 1	26	1.572	1.572	2 0 2	2

Table 8
Atomic coordinates ($\times 10^3$) for K_2AlF_5

Atom/site	*x*	*y*	*z*
K(1)/(2e)	0	$\frac{1}{2}$	$\frac{1}{2}$
Al(1)/(1a)	0	0	0
F(1)/(1b)	0	0	$\frac{1}{2}$
F(2)/(4j)	219	219	0

$a=5.965(1)$ Å, $c=3.699(1)$ Å, $Z=1$. No reflection condition was observed, leading to the space group *P*4/*mmm*. The cell parameters are related, with a small contraction, to those of the hydrated monoclinic form: $a_t \approx a_m$, $b_t \approx c_m$, $c_t \approx b_m/2$. This leads to the conclusion that the crystal structures of monohydrated and anhydrous K_2AlF_5 are virtually the same, except for the water molecules. Table 8 gives the atomic parameters of K_2AlF_5 deduced from those of $K_2AlF_5 \cdot H_2O$. The structure represented in Figs. 6 and 7 clearly shows the

Table 9
Interatomic distances (Å) and bond angles (°) for the $[AlF_6]$ octahedron in anhydrous K_2AlF_5

Al	F(2)	F(2)	F(2)	F(2)	F(1)	F(1)
F(2)	**1.847**	3.695	2.613	2.613	2.614	2.614
F(2)	180	**1.847**	2.613	2.613	2.614	2.614
F(2)	90	90	**1.847**	3.695	2.614	2.614
F(2)	90	90	180	**1.847**	2.614	2.614
F(1)	90	90	90	90	**1.849**	3.699
F(1)	90	90	90	90	180	**1.849**

Average⟨Al–F⟩ = 1.847 Å.

Table 10
Comparison between the cell parameters of the two forms of $K_2AlF_5 \cdot H_2O$ and anhydrous K_2AlF_5

m-$K_2AlF_5 \cdot H_2O$	*a* (Å): 6.133(3)	*b* (Å): 7.475(4)	*c* (Å): 6.142(3)	*β* (°): 97.17(2)	$Z=2$	*V* ($Å^3$): 279.4
o-$K_2AlF_5 \cdot H_2O$ [2]	*a* (Å): 9.200(3)	*c* (Å): 7.486(3)	*b* (Å): 8.119(4)		$Z=4$	*V* ($Å^3$): 559.2
o-$K_2AlF_5 \cdot H_2O$ [a]	*a* (Å): 6.135(3)	*b* (Å): 7.486(3)	*c* (Å): 6.135(3)	*β* (°): 97.14(2)	$Z=2$	*V* ($Å^3$): 279.6
Anhydrous K_2AlF_5	*a* (Å): 5.965(1)	*c* (Å): 3.699(1)	*a* (Å): 5.965(1)		$Z=1$	*V* ($Å^3$): 131.6

[a] On the basis of a monoclinic cell.

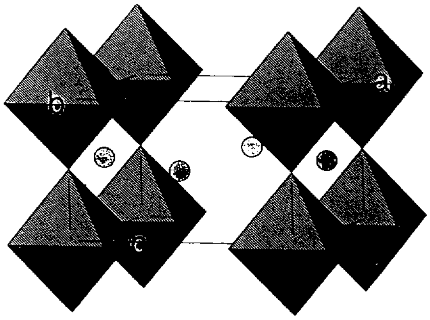

Fig. 6. Perspective view of the structure of anhydrous K_2AlF_5.

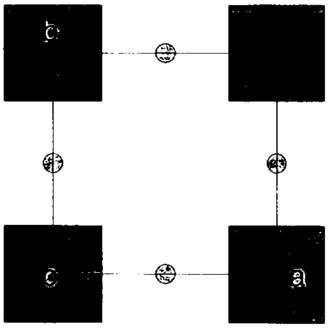

Fig. 7. The [001] projection of the structure of anhydrous K_2AlF_5.

same framework for the two compounds, with the water vacancy in the centre of the cell. Table 9 gathers together the interatomic distances and bond angles in the almost regular [AlF_6] octahedron. The potassium is 10-fold coordinated here with eight fluorine ions at 2.817 Å and two at 2.983 Å.

4. Discussion and conclusion

The crystal structure of monoclinic $K_2AlF_5 \cdot H_2O$ is closely related to that of the orthorhombic form [2]. Both can be described by the same atomic arrangements. The sole difference lies in the crystal symmetry, explained by the different temperature conditions of the hydrothermal syntheses: 350 °C for the *o*-form and 650 °C for the *m*-form, both under 1800 bar pressure. Relations between the cell parameters are clearly demonstrated by the results listed in Table 10. Comparison of the cell volumes shows that the *m*-form is the denser and so must correspond, at atmospheric pressure, to a low-temperature form as observed for the manganese compound. The two forms of $K_2AlF_5 \cdot H_2O$ are isostructural with those of $K_2MnF_5 \cdot H_2O$ [3,4]. The crystal structure of anhydrous K_2AlF_5 is also related to the previous ones minus the water molecules.

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