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Structures of two polymorphs of $MnF_3 \cdot 3H_2O$

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Abstract

From solutions of MnF_3 in hydrofluoric acid, $MnF_3 \cdot 3H_2O$ is formed in two polymorphic forms whose crystal structures were determined by X-ray diffraction on single crystals. Form **I**: space group $P2_1/c$, $Z=4$; lattice constants $a=8.413(1)$, $b=9.618(1)$, $c=6.370(1)$ Å, $\beta=97.71(1)°$; $R/wR=0.0417/0.0295$ for 710 reflections. Form **II**: space group $P2_1/a$, $Z=4$; lattice constants $a=8.481(7)$, $b=9.473(6)$, $c=6.473(4)$ Å, $\beta=100.51(6)°$; $R/wR=0.0303/0.0290$ for 650 reflections. In both polymorphs the structures consist of centrosymmetrical complex $[Mn(H_2O)_4F_2]^+$ cations and $[Mn(H_2O)_2F_4]^-$ anions. The cations exhibit very short Mn–F distances (**I**, 1.795 Å; **II**, 1.791 Å) in octahedra weakly elongated by the Jahn–Teller effect (Mn–O: **I**, 2.074/2.022 Å; **II**, 2.103/1.997 Å). The anions are strongly elongated along the $H_2O-Mn-OH_2$ axis (Mn–O: **I**, 2.19 Å; **II**, 2.15 Å. Mn–F: **I**, 1.837/1.842 Å; **II**, 1.837/1.856 Å). Both forms of $MnF_3 \cdot 3H_2O$ have approximately the same unit cell and very similar asymmetric units but they differ in the packing symmetry documented in the different space groups and, hence, in the networks of strong $O-H \cdots F$ hydrogen bonds ($O \cdots F$: 2.62 to 2.76 Å). In **I**, pure cation and pure anion layers alternate along [100] direction; in **II**, the corresponding layers have ordered mixed cation/anion composition.

Introduction

$MnF_3 \cdot 3H_2O$ was first prepared in 1824 by Berzelius [1]. Its solutions in aqueous HF are frequently used for preparing fluoromanganates(III). It has been supposed, by analogy with other trihydrates of metal trifluorides, that it is rhombohedral ($a=9.6$ Å, $c=9.8$ Å [2]), and that its structure contains $[Mn(H_2O)_6]^{3+}$ cations and $[MnF_6]^{3-}$ anions.

In the course of investigations on the interdependence of Jahn–Teller distortions in octahedral complex ions of Mn^{3+} (d^4-high-spin) and corresponding crystal structures, we became interested in the detailed structure of $MnF_3 \cdot 3H_2O$ and its hydrogen bond system. We report here the surprising results of X-ray single-crystal investigations.

Experimental

A solution of MnF_3 in 40% HF was left to evaporate for several days. Two different types of dark reddish-brown crystals were formed simultaneously,

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TABLE 1

Experimental crystallographic data for $MnF_3 \cdot 3H_2O$, forms **I** and **II**.

Compound	$MnF_3 \cdot 3H_2O$ (**I**)	$MnF_3 \cdot 3H_2O$ (**II**)
Molecular mass	165.98	165.98
Crystal size (mm)	appr. $0.1 \times 0.12 \times 0.18$	appr. $0.08 \times 0.12 \times 0.15$
Absorption	$\mu = 24.7$ cm^{-1} (no corr.)	$\mu = 24.7$ cm^{-1} (no corr.)
Space group	$P2_1/c$, $Z = 4$	$P2_1/a$, $Z = 4$
Cell parameters (Å) (Mo K_α)	$a = 8.413(1)$ $b = 9.618(1)$ $c = 6.370(1)$ $\beta = 97.71(1)°$	$a = 8.481(7)$ $b = 9.473(6)$ $c = 6.473(4)$ $\beta = 100.51(6)°$
Cell volume ($Å^3$)	510.8(1)	511.3(6)
Temperature (K)	293	293
Density (g cm^{-3})	$D_c = 2.16$	$D_c = 2.16$ g
Diffractometer	4-circle CAD 4 (Enraf–Nonius)	4-circle R3/V (Siemens)
Radiation	Mo K_α, graphite monochromator	
Scan mode	Ω-scan	
Scan width	$(0.9 + 0.35 \ tg\Theta)°$ and 25% before and after each reflexion for background	1.0°; stationary background measurement
Measuring range	$2° < \Theta < 23°$, $\pm h$, $+k$, $+l$	$1° < \Theta < 25°$, $\pm h$, $+k$, $+l$
Total of reflexions	1037	1512
Uniques	906; $650 > 3\sigma(F_o)$	1350; $710 > 3\sigma(F_o)$
Refinement	Prog. SHELXTL-*Plus* [13]	
Atomic form factors $\Delta f'$, $\Delta f''$	Extracted from ref. 14	
Extinction coefficient	$\epsilon = 3.5 \times 10^{-6}$	$\epsilon = 2.0 \times 10^{-6}$
	$F^* = F_c/(1 + \epsilon F_c^2/\sin 2\Theta)^{0.25}$	
R/wR	0.0417/0.0295 (69 parameters)	0.0303/0.0291 (69 parameters)
	$w = 1/\sigma^2(F_o)$	

which are now called forms **I** and **II**. There is no difference in colour or shape; the polymorphs were detected by X-ray investigation of single crystals only.

The investigations were made on several crystals by X-ray diffraction on four circle diffractometers. The experimental crystallographic data for the two forms are collected in Table 1. The structures were solved by Patterson methods and refined using anisotropic temperature factors for all non-H atoms. The H atom positions were found in subsequent difference Fourier syntheses, but were refined with restricted common O—H bond lengths of about 0.8 Å. In the last cycles of refinement, they were fixed on "riding" positions. The resulting atomic parameters are compiled in Table 2*.

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*Listings of anisotropic temperature factors and structure factors are available from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, under specification of deposit No. CSD-56304, authors and journal reference.

TABLE 2

Atomic parameters and equivalent isotropic temperature factors (isotropic temperature factors for H atoms) for $MnF_3 \cdot 3H_2O$, forms **I** and **II**

$$U_{eq} = 1/3(\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j)$$

Atom	x	y	z	U_{eq}/U
Mn1(I)	0.5	0.0	0.0	0.0200(4)
Mn1(II)	*0.5*	*0.0*	*0.0*	*0.0161(3)*
Mn2	0.0	0.0	0.5	0.0197(4)
	0.0	*0.0*	*0.5*	*0.0158(3)*
F1	0.3015(4)	0.0596(4)	0.0543(5)	0.0344(11)
	0.2997(3)	*0.0497(3)*	*0.0453(4)*	*0.0269(8)*
F2	0.5400(4)	−0.0751(4)	0.2671(5)	0.0339(12)
	0.5339(3)	*−0.1042(2)*	*0.2470(4)*	*0.0291(9)*
F3	−0.0956(4)	0.1475(3)	0.3642(5)	0.0355(11)
	−0.0837(3)	*0.1483(2)*	*0.3464(4)*	*0.0264(8)*
O1	0.6152(5)	0.1952(4)	0.1143(7)	0.0372(14)
	0.6036(4)	*0.1845(3)*	*0.1629(5)*	*0.0314(10)*
H11	0.5595	0.2374	0.1771	0.057(9)
	0.5626	*0.2366*	*0.2240*	*0.056(7)*
H12	0.6901	0.1843	0.1967	0.057(9)
	0.6883	*0.1833*	*0.2248*	*0.056(7)*
O2	0.0367(5)	0.1053(4)	0.7866(6)	0.0383(15)
	0.0477(4)	*0.1208(3)*	*0.7566(4)*	*0.0317(11)*
H21	0.1128	0.1035	0.8691	0.057(9)
	0.1174	*0.1084*	*0.8455*	*0.056(7)*
H22	−0.0049	0.1726	0.8156	0.057(9)
	0.0422	*0.2004*	*0.7524*	*0.056(7)*
O3	0.2141(5)	0.0709(5)	0.4342(6)	0.0433(16)
	0.2277(3)	*0.0471(3)*	*0.4327(4)*	*0.0318(11)*
H31	0.2427	0.0564	0.3262	0.057(9)
	0.2541	*0.0323*	*0.3295*	*0.056(7)*
H32	0.2893	0.0545	0.5132	0.057(9)
	0.3066	*0.0548*	*0.5079*	*0.056(7)*

Results and discussion

$MnF_3 \cdot 3H_2O$ shows very special polymorphic behaviour: both forms are formed under the same conditions, have nearly the same unit cells, and have the same space group type. The greatest difference in the lattice constants is 1.6%, the monoclinic angle β deviates by 2.8%. Both phases have been found to be present in all powder patterns. Single-crystal investigations on several crystals of the same preparation clearly revealed the existence of two species, distinguishable by the different orientation of the glide planes. If the unit cell is set up with the most similar values for both forms (Table 1), for **I** the $P2_1/c$ space group is found and for **II** the $P2_1/a$ setting has to be chosen according to the systematic extinctions.

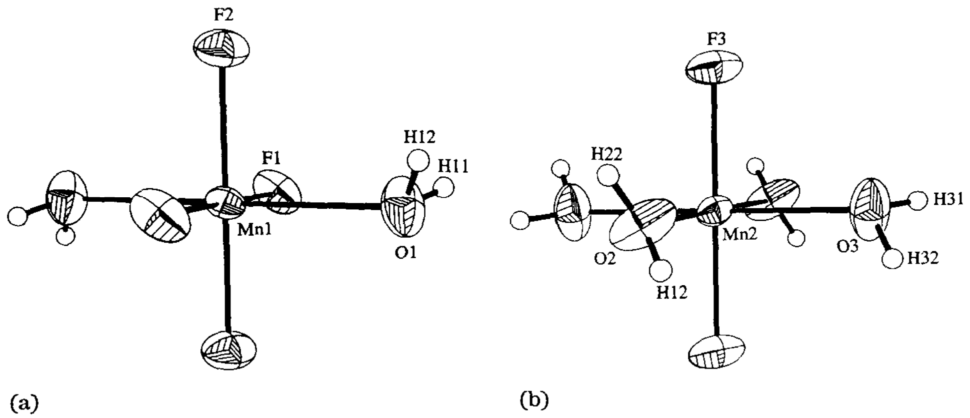

Fig. 1. Coordination polyhedra of (a) the $[Mn(H_2O)_2F_4]^-$ anion and the (b) $[Mn(H_2O)_2F_4]^+$ cation in $MnF_3 \cdot 3H_2O$ (I).

The results of the refinement of both structures are rather similar if we look at the asymmetric units only. Located on centres of symmetry, a $[Mn(H_2O)_4F_2]^+$ cation at 0,0,0.5 and an $[Mn(H_2O)_2F_4]^-$ anion at 0.5,0,0 are found with similar orientations in both structures (Table 2 and Figs. 1 and 2).

Isolated $[Mn(H_2O)_2F_4]^-$ anions are already known from the alkali compounds $CsMnF_4 \cdot 2H_2O$ [3–5] or $NaMnF_4 \cdot 3H_2O$ [6]. As in these, the $Mn-OH_2$ bonds in the anion of $MnF_3 \cdot 3H_2O$ undergo an elongation by the Jahn–Teller effect (Table 3). The distortion is significantly weaker in form **II** [Mn–O, 2.145(3) Å] than in **I** [2.192(4) Å], probably because of the different hydrogen bonds (see below).

The centrosymmmetrical $[Mn(H_2O)_4F_2]^+$ cation (with Mn2; see Table 3 and Fig. 1) has not been previously described. In both polymorphs, it has a very short F–Mn–F axis with Mn–F distances of 1.795(3) Å (I) or 1.791(3) Å (II). It may be compared with the short terminal Mn–F bonds in $AMnF_4$ layered compounds [7]. The weak equatorial bonds towards the four aqua ligands are formally replaced there by comparable weak bonds towards the bridging fluorine atoms. The Jahn–Teller distortion in the $[Mn(H_2O)_4F_2]^+$ cations is relatively small. The equatorial Mn–O bonds split into longer (*I*, 2.074 Å; **II**, 2.103 Å) and shorter bonds (**I**, 2.022 Å; **II**, 1.997 Å). The angular distortion is weak in both the cations and the anions. There is a distorted CsCl type of arrangement of cations and anions (Mn···Mn, 4.84 to 5.78 Å).

Hydrogen bonds

The main difference between the two polymorphs concerns the packing of cations and anions in the layers parallel to the *bc* plane (Fig. 2). In **I**, cations only are arranged in the *bc* planes at $x=0$, 1, ... and pure anionic layers are at $x=0.5$, 1.5, ... In **II**, mixed cation/anion layers are stacked in

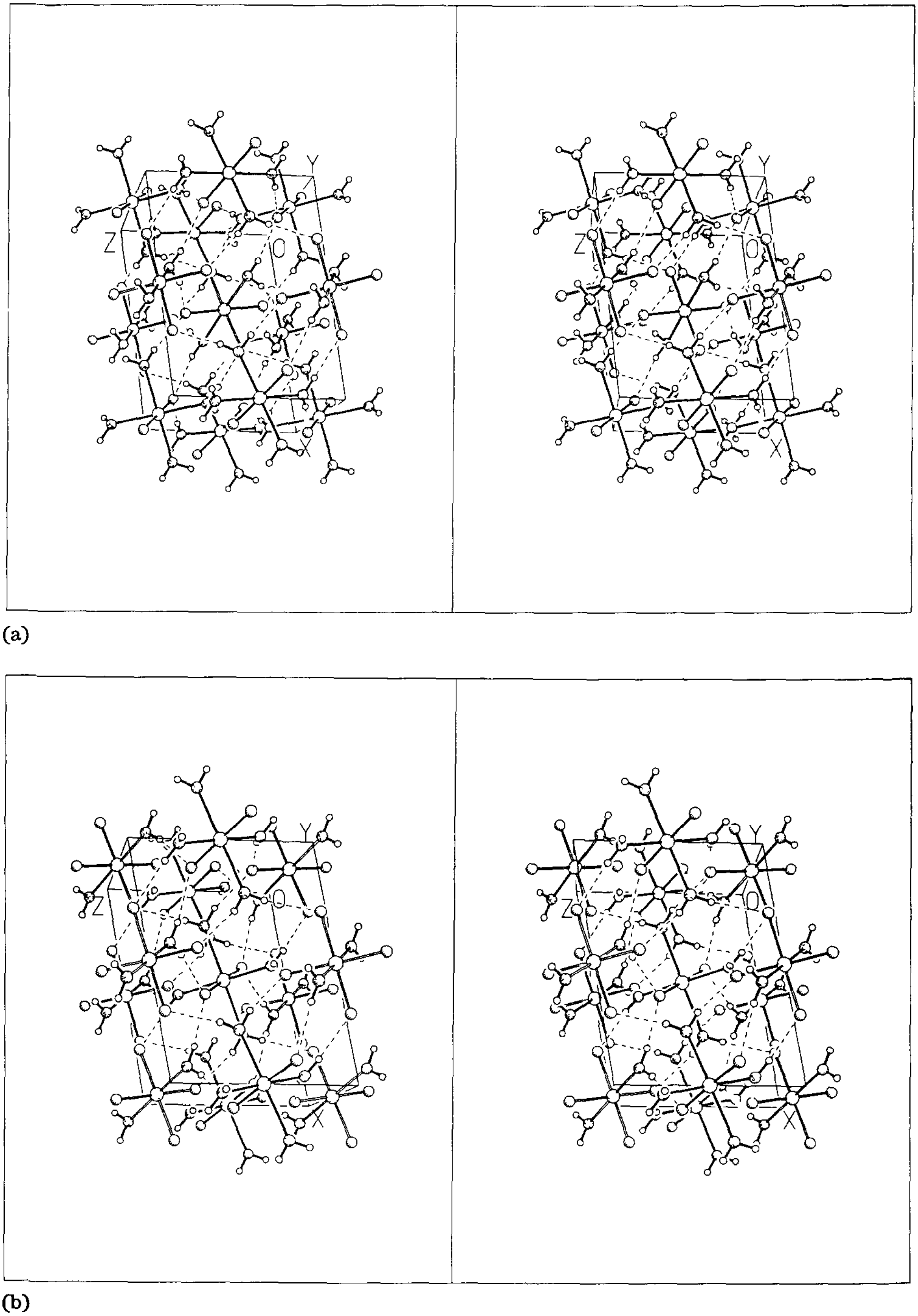

Fig. 2. Stereo view, projected from the [010] direction, of (a) form **I**, and (b) form **II** of $MnF_3 \cdot 3H_2O$. Cations (Mn2) are drawn with dark bonds and anions with light bonds.

TABLE 3

Bond lengths (Å) and angles (°) in MnF_3 $3H_2O$, forms **I** and **II**

Mn1(I)−F2, F2^{a}	1.837(3)	Mn2(I)−F3, F3^{b}	1.795(3)
Mn1(II)−	*1.856(3)*	*Mn2(II)−*	*1.791(3)*
Mn1−F1, F1^{a}	1.842(3)	Mn2−O3, O3^{b}	2 022(4)
	1.837(3)		*2.103(3)*
Mn1−O1, O1^{a}	2.192(4)	Mn2−O2, O2^{b}	2.074(4)
	2 145(3)		*1.997(3)*
F1−Mn1−O1^{a}	87.6(2)	F3−Mn2−O2^{b}	87.6(2)
	88.8(1)		*89.3(1)*
F2−Mn1−O1^{a}	89.4(2)	O3−Mn2−O2	89.2(2)
	88.6(1)		*89 8(1)*
F2−Mn1−F1^{a}	89 6(1)	F3−Mn2−O3	89.3(2)
	89.9(1)		*90.3(1)*
F2−Mn1−F1	90.4(1)	F3−Mn2−O3^{b}	90.7(2)
	90 1(1)		*89.7(1)*
F2−Mn1−O1	90.6(2)	O3−Mn2−O2^{b}	90.8(2)
	91.4(1)		*90.2(1)*
F1−Mn1−O1	92.5(2)	F3−Mn2−O2	92.4(2)
	91 2(1)		*90 7(1)*

Symmetry operations $^{a}1-x,\ -y,\ -z$; $^{b}-x,\ -y,\ 1-z$.

TABLE 4

Geometry of hydrogen bonds in $MnF_3\cdot 3H_2O$, forms **I** and **II**: Bond distances (Å) and angles (°)

Donator	H	Acceptor	D−H	D···A	H···A	D−H···A
O1(I)	H11	F2^{a}	0.771	2.725	2.040	148
O1(II)	*H11*	*F3*^{d}	*0 756*	*2.671*	*1.927*	*168*
O1	H12	F3^{b}	0.771	2.761	1.999	169
		F3^{b}	*0.756*	*2.722*	*1.978*	*168*
O2	H21	F1^{c}	0.772	2.654	1.894	168
		F1^{c}	*0.756*	*2 657*	*1.909*	*171*
O2	H22	F3^{d}	0.770	2.699	1.932	173
		F2^{f}	*0.756*	*2.695*	*1.961*	*164*
O3	H31	F1	0.771	2.624	1.864	168
		F1	*0.756*	*2.687*	*1.954*	*163*
O3	H32	F2^{e}	0.770	2.617	1.877	161
		F2^{e}	*0 756*	*2.674*	*1.945*	*162*

Symmetry operations: $^{a}1-x,\ 1/2+y,\ 1/2-z$; $^{b}1+x,\ y,\ z$; $^{c}x,\ y,\ z+1$; $^{d}x,\ 1/2-y,\ 1/2+z$; $^{e}1-x,\ -y,\ 1-z$; $^{f}-x,\ 1/2+y,\ 1/2-z+1$.

the [100] direction. Thus, in **I** the shortest Mn···Mn distances (5.77 Å) are cation–cation (or anion–anion) distances; in **II** the low values for Mn···Mn of 5.74 Å are between cations and anions. This may be understood by looking at the different hydrogen bond systems. Every water molecule makes two hydrogen bonds towards the fluorine atoms (six per formula unit). In **I**, one of these is an "in-plane" O—H···F bond from cation to cation (Fig. 2 and Table 4); the other five hydrogen bonds are between the layers. In **II**, all hydrogen bonds connect cations and anions only. There are no hydrogen bonds between anions and anions and no O—H···O hydrogen bonds. Every F atom uses two acceptor functions for hydrogen bonds.

There is a correlation between the Mn—OH_2 distances and the strength of O—H···F hydrogen bonds, found also in other fluoride hydrate systems [8]: short Mn—O bonds give short O—H···F hydrogen bonds and the converse is true for longer Mn—O bonds. In the cations of **I**, Mn2—O3 are the shorter Mn—O bonds, and the hydrogen bonds from O3 to F2 and F1 are the shortest (O···F, 2.62 Å). In **II**, Mn2—O2 is the shortest bond, and O2···F1 makes the shortest hydrogen bond.

Jahn–Teller ordering

The orientation of the Jahn–Teller-distorted octahedral groups is different for each polymorph. In **I**, the cationic (100) layers ($x = 0$) show ferro-distortive order with orientation of the elongated Mn—OH_2 axes approximately perpendicular to the plane. The anionic layers ($x = 0.5$) have strongly angular antiferro-distortive order, approximately within the plane. In **II**, in the mixed cation/anion (100) layers, we find angular antiferro-distortive order in both planes (at $x = 0$ and 0.5).

Structural relations

The structures of the both polymorphs of $MnF_3 \cdot 3H_2O$ are not related to the hitherto known two types of structures of other $MF_3 \cdot 3H_2O$ compounds [9]. In the rhombohedral type of structures, found for example in $CrF_3 \cdot 3H_2O$ [9, 10] and proposed for many other trihydrates [9], disordered $[M(H_2O)_3F_3]$ molecules are postulated but disordered ion pairs like $[M(H_2O)_6]^{3+}/[MF_6]^{3-}$ are also discussed [2, 9]. Thus, intermediate ion pairs $[M(H_2O)_4F_2]^+/[M(H_2O)_2F_4]^-$ are also possible in those disordered systems. Probably, the former samples of $MnF_3 \cdot 3H_2O$, indexed with a rhombohedral cell ($a = 9.6$ Å, $c = 9.8$ Å [2]) are identical with ours. If we disregard small splitting of lines, the powder pattern of our sample may be indexed quite satisfactorily with this cell. The second tetragonal structure type, found for example in $InF_3 \cdot 3H_2O$ [11] and β-$AlF_3 \cdot 3H_2O$ [12], exhibits linear chains of disordered $[M(H_2O)_2F_4]$ octahedra sharing *trans*-F ligands and an additional water of crystallization molecule. The preference of the unique structures of $MnF_3 \cdot 3H_2O$ must be attributed to the d^4 configuration of Mn^{3+}, for which tetragonally elongated groups like the $[Mn(H_2O)_2F_4]^-$ anions obtain additional stabilization from the Jahn–Teller effect.

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