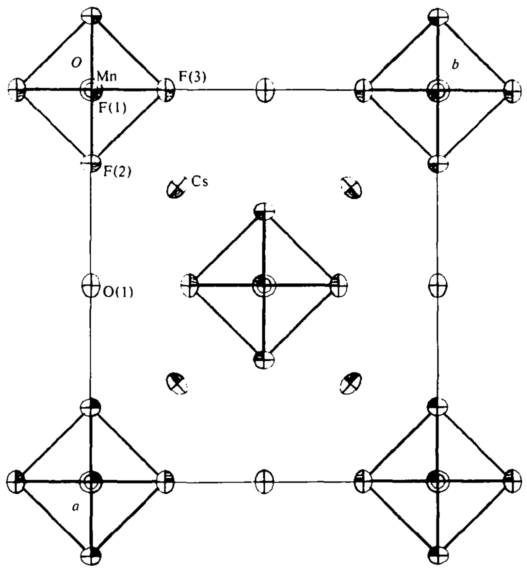

Fig. 1. Projection of the structure along the c axis.

Water molecules are statistically distributed on four-fold mm sites with an occupancy of $\frac{1}{2}$. A similar situation has been found in the crystal structure of $Pd(NH_3)_4Cl_2.H_2O$ (Bell, Bowles, Cumming, Hall & Holland, 1976).

There are ten F atoms around the Cs atom, with bond lengths of 3·098–3·260 Å. Additionally, four O sites are located 3·397 Å from Cs, so that the effective coordination number of Cs is twelve.

The authors wish to thank Professor L. Golič for valuable discussions and for his interest in this work.

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Acta Cryst. (1978). B**34**, 3339–3341

Rubidium Pentafluoromanganate(III) Monohydrate

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(*Received* 24 *May* 1978; *accepted* 10 *July* 1978)

Abstract. $Rb_2MnF_5.H_2O$, orthorhombic, $Cmcm$, a = 9·383 (2), b = 8·214 (3), c = 8·348 (2) Å, Z = 4, D_c = 3·498 g cm^{-3}, V = 643·397 Å^3, μ(Mo $K\alpha$) = 180·6 cm^{-1}. The stoichiometry is achieved by the sharing of opposite vertices of MnF_6 octahedra to form infinite kinked anionic chains. The octahedra are (because of the Jahn–Teller effect) elongated in the chain direction.

Introduction. In the previous paper we described the crystal structure of $Cs_2MnF_5.H_2O$. For Rb, only the preparation of Rb_3MnF_6 has been mentioned previously (Siebert & Hoppe, 1972). Here we report the synthesis and crystal structure of $Rb_2MnF_5.H_2O$.

Mn^{III} oxide (0·01 mol) was dissolved in 20% HF (10 cm^3), and a solution of RbF (0·04 mol in 20 cm^3 of 20% HF) was added. The resulting violet crystals were filtered off, washed with methanol and dried in a vacuum desiccator over KOH. (Composition: found: Mn 16·47, Rb 50·25, F 27·8, H_2O 4·92%; calculated for $Rb_2MnF_5.H_2O$: Mn 16·21, Rb 50·44, F 28·03, H_2O 5·32%.) The procedure was repeated with Rb:Mn molar ratios of 5, 10 and 20 to 1. Increasing the amount of RbF resulted in precipitation of the required complex.

Preliminary cell dimensions and the space-group symmetry were determined from rotation and Weissenberg photographs (Cu $K\alpha$ radiation). Data were collected with an Enraf–Nonius CAD-4 automatic diffractometer in the ω–2θ mode, using a graphite monochromator and Mo $K\alpha$ radiation. Accurate cell constants were determined from a least-squares fit of 30 high-angle reflections. A crystal 0·03 × 0·17 × 0·31 mm was used. 3735 intensities were measured in the range 1·5 ≤ θ ≤ 30·0°. Lorentz–polarization and absorption corrections were made. After averaging equivalent reflections (mean discrepancy on $I = 4{\cdot}0\%$), 422 reflections with $I_o \geq 3\sigma(I_o)$ were obtained.

The position of the Rb atom was determined by the heavy-atom method. The coordinates of the other non-hydrogen atoms were obtained from a three-dimensional F_o Fourier synthesis. Refinement of positional and isotropic thermal parameters gave an R value of 0·051. The structure was then refined by a number of least-squares cycles with anisotropic temperature factors. A difference electron density map revealed the positions of the H atoms. These atoms were included in the refinement as invariants with isotropic thermal parameters (U = 0·05 Å^2). An extinction parameter (Larson, 1967) was also included and its final value was $1{\cdot}04 \times 10^{-3}$. The weighting function was determined empirically [weight $(F_{obs}) = wF \times wS$]:

$F_{obs} < 60$:	$wF = (F_{obs}/60)^{2\cdot0}$
$F_{obs} > 100$:	$wF = (100/F_{obs})^{2\cdot0}$
$60 \leq F_{obs} \leq 100$:	$wF = 1\cdot0$
$\sin\theta < 0\cdot26$:	$wS = (\sin\theta/0\cdot26)^{2\cdot0}$
$\sin\theta > 0\cdot36$:	$wS = (0\cdot36/\sin\theta)^{2\cdot0}$
$0\cdot26 \leq \sin\theta \leq 0\cdot36$:	$wS = 1\cdot0$.

Refinement terminated at $R_1 = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}| = 0{\cdot}018$, and $R_2 = [\sum w(F_{obs} - F_{calc})^2/\sum wF^2_{obs}]^{1/2} = 0{\cdot}016$. Atomic scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for other atoms from Cromer & Mann (1968). Those of non-hydrogen atoms were corrected for the effects of anomalous scattering (Cromer & Liberman, 1970).

The calculations were performed on a CDC Cyber 72 computer using the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).*

Discussion. The final atomic coordinates are listed in Table 1. The structural arrangement is illustrated in Figs. 1 and 2. Mn atoms are octahedrally coordinated by six F atoms. The octahedra are linked through *trans* F atoms to form endless kinked anionic chains [Mn—F—Mn 175·4 (2)°], parallel to the c axis. The Rb cations and water molecules are located on special positions between the anionic chains.

Interatomic distances and angles are given in Table 2. There are two long and four short bonds around the Mn atom, which is characteristic of high-spin Mn^{III} compounds (Bukovec & Kaučič, 1977; Stults, Marianelli & Day, 1975). The difference between the two short Mn—F lengths is due to the formation of hydrogen bonds between F(3) and water molecules.

The crystal structure of $Rb_2MnF_5.H_2O$ can also be described as a distorted cubic close-packed arrange-

Table 1. *Final atomic coordinates*

	x	y	z
Rb	0·21604 (4)	0·28333 (5)	0·25
Mn	0·00	0·00	0·00
F(1)	0·00	0·01025 (53)	0·25
F(2)	0·19558 (24)	0·00	0·00
F(3)	0·00	0·22640 (27)	−0·00669 (31)
O(1)	0·50	0·04807 (56)	0·25
H(1)	0·50	0·1403	0·1531

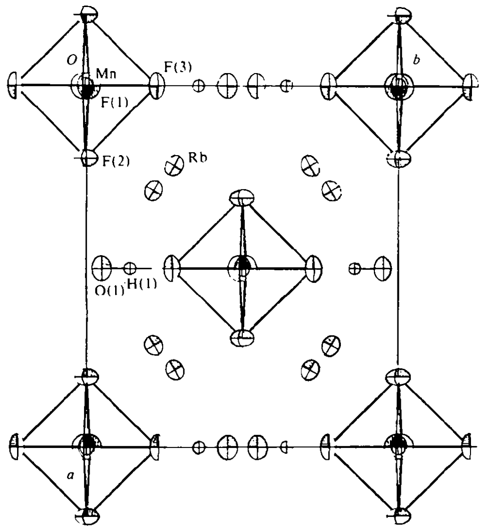

Fig. 1. Projection of the structure along the c axis.

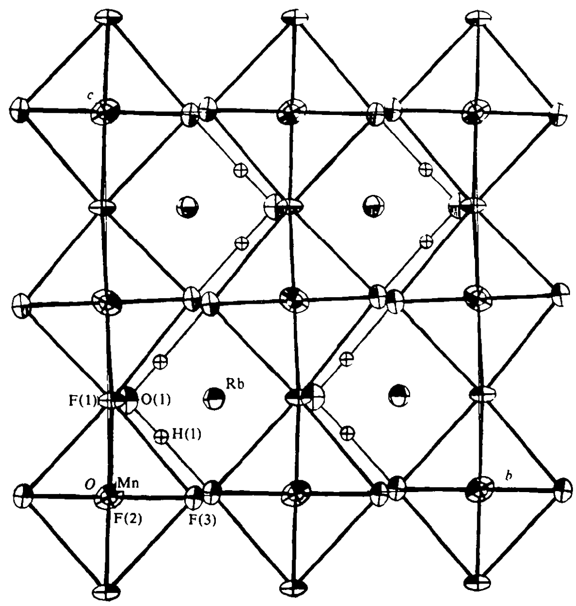

Fig. 2. Projection of the structure along the a axis.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33763 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Mn octahedron

Mn–F(1)	2·089 (1)	F(1)–Mn–F(2)	90·0 (0)
Mn–F(2)	1·835 (2)	F(1)–Mn–F(3)	89·4 (1)
Mn–F(3)	1·860 (2)	F(2)–Mn–F(3)	90·0 (0)

Hydrogen bonds

O(1)–$F(3^{i})$,$F(3^{ii})$	2·749 (4)

Rb polyhedron

Rb–F(1)	3·023 (3)	Rb–$F(2^{i})$,$F(2^{ii})$	2·865 (1)
Rb–F(2),$F(2^{iii})$	3·132 (1)	Rb–$F(3^{i})$,$F(3^{ii})$	3·351 (2)
Rb–F(3),$F(3^{iii})$	2·987 (2)	Rb–O(1)	3·291 (3)
Rb–$F(1^{iv})$	3·252 (3)	Rb–$O(1^{v})$	2·973 (4)

O polyhedron

O(1)–Rb^{vi},Rb^{vii}	2·973 (4)
O(1)–Rb^{iii},Rb^{viii}	3·291 (3)
O(1)–F(2),$F(2^{iii})$,$F(2^{viii})$,$F(2^{ix})$	3·560 (2)
O(1)–$F(3^{vi})$,$F(3^{vii})$	3·402 (4)
O(1)–$F(3^{i})$,$F(3^{ii})$	2·749 (4)

Equivalent positions

(i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$	(vi) $\frac{1}{2}+x, -\frac{1}{2}+y, z$
(ii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$	(vii) $\frac{1}{2}+x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iii) $x, y, \frac{1}{2}-z$	(viii) $1-x, y, z$
(iv) $\frac{1}{2}+x, \frac{1}{2}+y, z$	(ix) $1-x, -y, \frac{1}{2}+z$
(v) $-\frac{1}{2}+x, \frac{1}{2}+y, z$	

ment of Rb, F and O atoms, with Mn atoms in the octahedral holes. The distances in the Rb and O polyhedra are presented in Table 2.

$Rb_2MnF_5.H_2O$ is isostructural with $K_2AlF_5.H_2O$ (Brosset, 1942). The crystal structure of the Al compound is of low accuracy and the position of the water molecule was determined only approximately.

The bond lengths and the Mn–F–Mn angles in $Rb_2MnF_5.H_2O$ and $Cs_2MnF_5.H_2O$ are compared with those in $K_2MnF_5.H_2O$ (Edwards, 1971) in Table 3.

Table 3. *Comparison of some bond distances* (Å) *and angles* (°) *in* $M^{I}_{2}MnF_5.H_2O$

F(1) is bridging; F(2) and F(3) are terminal.

	Mn–F(1)	Mn–F(2)	Mn–F(3)	Mn–F(1)–Mn
$K_2MnF_5.H_2O$	2·072	1·821	1·842	163·3
$Rb_2MnF_5.H_2O$	2·089	1·835	1·860	175·4
$Cs_2MnF_5.H_2O$	2·127	1·835	1·868	180·0

There is a lengthening of Mn–F bond distances, as well as a reduction in the tilting of the octahedra, as a result of increasing the size of the cation.

The authors thank Professor L. Golič for many helpful discussions.

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Acta Cryst. (1978). B**34**, 3341–3343

Structure de l'Hexachlorure de Cadmium–Calcium Dodécahydraté

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(*Reçu le* 28 *avril* 1978, *accepté le* 18 *juillet* 1978)

Abstract. $CdCa_2Cl_6.12H_2O$, $P2_1/c$, $a = 8{\cdot}839\ (2)$, $b = 10{\cdot}106\ (2)$, $c = 12{\cdot}714\ (4)$ Å, $\beta = 114{\cdot}21\ (3)°$, $V = 1035{\cdot}82$ Å^3, $Z = 2$, $D_c = 2{\cdot}10$ g cm^{-3}, μ(Mo $K\alpha$) = 24·5 cm^{-1}. This compound and β-$CaCl_2.4H_2O$ are isomorphous. Cd is surrounded by six Cl atoms and Ca is surrounded by one Cl and seven water molecules.

Introduction. Les considérations faites au laboratoire sur les structures des hydrates des chlorures de cadmium et de calcium nous ont conduits à entreprendre les déterminations de structures relatives aux chlorures doubles hydratés de ces deux cations.

Les cristaux faisant l'objet de la présente étude ont