

Fig. 1. Projection de l'arrangement atomique de $\text{Ag}_2\text{Cr}_2\text{O}_7$ sur le plan ab .

les principales distances interatomiques et angles de liaison dans cet arrangement.

Discussion. Les Figs. 1 et 2 fournissent deux projections de cet arrangement atomique essentiellement formé d'un enchaînement tridimensionnel d'anions Cr_2O_7 et d'octaèdres AgO_6 assez déformés. L'anion Cr_2O_7 est caractérisé par un angle $\text{Cr}(1)\text{—O}(L)\text{—Cr}(2)$ de $121,6^\circ$ inférieur à la moyenne des angles de ce type observés dans les groupements Cr_2O_7 ($130,3^\circ$) (Löfgren, 1974). Par contre les moyennes des distances Cr—O observées dans les deux tétraèdres de l'anion [$1,670 \text{ \AA}$ pour le tétraèdre $\text{Cr}(1)\text{O}_4$ et $1,675 \text{ \AA}$ pour

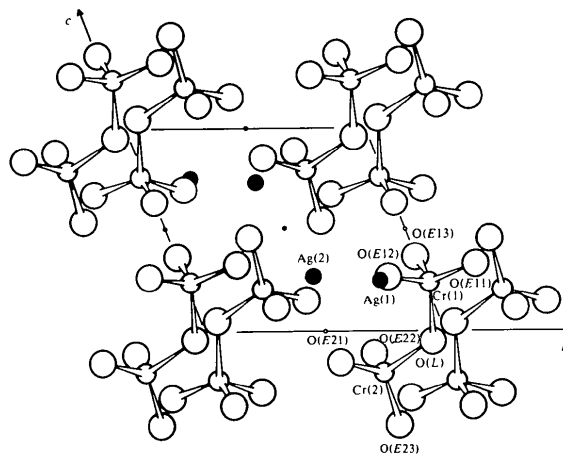


Fig. 2. Projection de l'arrangement atomique de $\text{Ag}_2\text{Cr}_2\text{O}_7$ sur le plan bc .

$\text{Cr}(2)\text{O}_4$] sont nettement plus élevées que la moyenne des distances Cr—O ($1,652 \text{ \AA}$) observée dans les anions de ce type (Löfgren, 1974). Ce fait peut probablement s'expliquer en remarquant que la moitié des atomes d'oxygène des tétraèdres CrO_4 est reliée par des liaisons de longueurs normales à deux atomes d'argent.

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Caesium Pentafluoromanganate(III) Monohydrate

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Abstract. $\text{Cs}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$, orthorhombic, $Cmmm$, $a = 9.727(8)$, $b = 8.686(11)$, $c = 4.254(2) \text{ \AA}$, $Z = 2$, $D_c = 4.005 \text{ g cm}^{-3}$, $V = 359.415 \text{ \AA}^3$, $\mu(\text{Mo } K\alpha) = 120.8 \text{ cm}^{-1}$. The structure consists of tetragonally elongated MnF_6 octahedra linked through *trans*-bridging F atoms to give infinite chains of composition $(\text{MnF}_5)_n^{2n-}$ parallel to the c axis, Cs atoms and water molecules. The water molecule appears to be disordered over positions in the vicinity of $(\frac{1}{2}, 0, \pm \frac{1}{4})$; the occupancy

of the site is only one half with respect to space group $Cmmm$.

Introduction. There are two hydrated caesium fluoromanganates(III), which can be prepared from aqueous solutions of the corresponding fluorides. The crystal structure of $\text{Cs}[\text{MnF}_4(\text{H}_2\text{O})_2]$ has recently been solved (Bukovec & Kaučič, 1977). The compound comprises $[\text{MnF}_4(\text{H}_2\text{O})_2]^-$ octahedra interlinked by hydrogen

bonds in three dimensions. Tetragonal elongation of the octahedra due to the Jahn–Teller effect has also been observed. Only the synthesis of $\text{Cs}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$ has been mentioned previously (Riss & Vituhnovskaja, 1958). We now report the crystal structure of this compound.

Single crystals of $\text{Cs}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$ were obtained by the slow evaporation of an aqueous solution containing CsF and MnF_3 in the molar ratio 50:1. Preliminary unit-cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs taken with $\text{Cu } K\alpha$ radiation. Accurate cell parameters were derived by the least-squares analysis of the positions of 30 high-angle reflections, collected on an Enraf–Nonius CAD-4 automatic diffractometer, equipped with a graphite monochromator and $\text{Mo } K\alpha$ radiation. Intensity data were then recorded with the ω – 2θ scan. The whole sphere of reflection (2084 in all) in the range $1.5 \leq \theta \leq 30.0^\circ$ was measured. The symmetry-related reflections were averaged (mean discrepancy on $I = 9.9\%$) to yield 321 independent reflections of which 303 with $I_o \geq 3\sigma(I_o)$ (from counting statistics) were considered observed and used for the structure analysis. Structure amplitudes were derived by the application of Lorentz, polarization and absorption ($\mu r = 0.9$) corrections.

The position of the Cs atom was obtained from a three-dimensional Patterson function, while the subsequent electron density map gave coordinates for all non-hydrogen atoms. There are two O atoms in the unit cell; however, the maximum which may correspond to O was located in the vicinity of a fourfold position. By refining the population parameters, that of O fell to a value of 0.4. At the same time, the isotropic temperature factor of O, which was unusually high (0.18 \AA^2), diminished to the normal value of 0.039 \AA^2 . The structure was then refined with anisotropic temperature factors and an O population parameter of 0.5 to final agreement indices of $R_1 = \sum |F_{\text{obs}}| - |F_{\text{calc}}| / \sum |F_{\text{obs}}| = 0.058$, and $R_2 = [\sum w(F_{\text{obs}} - F_{\text{calc}})^2 / \sum wF_{\text{obs}}^2]^{1/2} = 0.043$. Atomic scattering factors for neutral Cs, Mn, F and O (Cromer & Mann, 1968) and for neutral H (Stewart, Davidson & Simpson, 1965) together with anomalous-scattering coefficients f' and f'' for all non-hydrogen atoms (Cromer & Liberman, 1970) were used in F_{calc} . An extinction parameter (Larson, 1967) was included in the refinement, and its final value was 3.72×10^{-3} . The following weighting scheme [weight (F_{obs}) = $wF \times wS$] was used:

$$\begin{aligned} F_{\text{obs}} < 50: & \quad wF = (F_{\text{obs}}/50)^{2.0} \\ F_{\text{obs}} > 80: & \quad wF = (80/F_{\text{obs}})^{3.0} \\ 50 \leq F_{\text{obs}} \leq 80: & \quad wF = 1.0 \\ \sin \theta < 0.38: & \quad wS = (\sin \theta / 0.38)^{2.0} \\ \sin \theta > 0.46: & \quad wS = (0.46 / \sin \theta)^{3.0} \\ 0.38 \leq \sin \theta \leq 0.46: & \quad wS = 1.0. \end{aligned}$$

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

Discussion. The final positional parameters are given in Table 1, while interatomic distances and angles are listed in Table 2. Each Mn atom has an octahedral coordination of F atoms. The octahedra share their *trans* vertices to form endless anionic chains parallel to the *c* axis, with an Mn–F–Mn angle of 180.0° (Fig. 1). As shown by the Mn–F bond lengths, the octahedra are tetragonally elongated in the direction of the bridging F atoms. The distortion is ascribed to the operation of the Jahn–Teller effect, characteristic of high-spin Mn^{III} compounds. The short and long Mn–F bond distances are within the limits known for fluoromanganates (III) (Bukovec & Kaučič, 1977; Stults, Marianelli & Day, 1975). There is also a difference between the two equatorial Mn–F bond lengths; this is because the F(3) atoms form relatively strong hydrogen bonds [O–F(3) 2.739 Å]. The F–Mn–F angles are all 90.0 or 180.0° .

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33764 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates*

	x	y	z
Cs	0.25	0.25	0.00
Mn	0.00	0.00	0.50
F(1)	0.00	0.00	0.00
F(2)	0.1887 (10)	0.00	0.50
F(3)	0.00	0.2150 (10)	0.50
O	0.50	0.00	0.2246 (89)

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

Mn octahedron			
Mn–F(1)	2.127 (1)	Mn–F(3)	1.868 (9)
Mn–F(2)	1.835 (10)		
Hydrogen bond			
O(1)–F(3 ^{III})	2.739 (18)		
Cs polyhedron			
Cs–F(1), F(1 ^I)	3.260 (2)		
Cs–F(2), F(2 ^{III}), F(2 ^{IV}), F(2 ^V)	3.098 (3)		
Cs–F(3), F(3 ^{III}), F(3 ^{IV}), F(3 ^V)	3.245 (2)		
Cs–O(1), O(1 ^{II}), O(1 ^{IV}), O(1 ^V)	3.397 (11)		
Equivalent positions			
(i)	$\frac{1}{2} + x, \frac{1}{2} + y, z$	(iv)	$\frac{1}{2} - x, \frac{1}{2} - y, -z$
(ii)	$-\frac{1}{2} + x, \frac{1}{2} + y, z$	(v)	$x, y, -z$
(iii)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$		

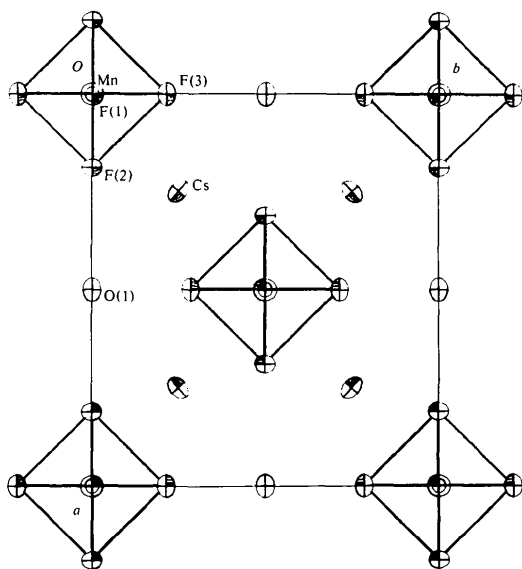


Fig. 1. Projection of the structure along the *c* axis.

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 $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Bell, Bowles, Cumming, Hall & Holland, 1976).

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Rubidium Pentafluoromanganate(III) Monohydrate

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Abstract. $\text{Rb}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$, 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 , $\mu(\text{Mo } K\alpha) = 180.6$ 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 $\text{Cs}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$. 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 $\text{Rb}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$.

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 $_2$ O 4.92%; calculated for $\text{Rb}_2\text{MnF}_5 \cdot \text{H}_2\text{O}$: Mn 16.21, Rb 50.44, F 28.03, H $_2$ O 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.

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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 $1.5 \leq \theta \leq 30.0^\circ$. Lorentz–polarization and