Synthesis and Crystal Structure of Caesium Diaquatetrafluoromanganate(III) [†]

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The complex $Cs[MnF_4(OH_2)_2]$, isolated from an aqueous solution of the corresponding fluorides, crystallizes in space group $C2/c$ with $a = 11.907(2)$, $b = 6.597(1)$, $c = 9.316(2)$ Å, $\beta = 121.77(1)°$, and $Z = 4$. The structure, solved by the heavy-atom method from X-ray diffractometer data (835 reflections), has been refined by least-squares techniques to R 0.024. The $[MnF_4(OH_2)_2]^{2-}$ anion is a tetragonally elongated octahedron, with equatorial Mn–F bond lengths of 1.846(2) and 1.847(2) Å respectively, and Mn–O 2.211(2) Å. The anions are interlinked by hydrogen bonds. Infrared data are also presented and tentatively assigned.

THE known fluoro-complexes of Mn^{III} are mainly anhydrous compounds of the anions $[MnF_6]^{3-}$, $[MnF_5]^{2-}$, and $[MnF_4]^{-}$.[1] Two hydrates have also been reported, *viz.* $K_2[MnF_5]\cdot H_2O$ [2] and $Cs_2[MnF_5]\cdot H_2O$.[3] In the potassium complex the water molecule is not co-ordinated, and the $[MnF_6]^{3-}$ octahedra share their *trans* vertices. For the caesium complex, only the synthesis was briefly reported. The stoicheiometry $M^IM^{III}F_4\cdot 2H_2O$ is often found in the literature, but not for manganese.

We now report the synthesis and crystal structure of $Cs[MnF_4(OH_2)_2]$. During the preparation of this paper, the crystal structure of rubidium diaquatetrafluorovanadate(III) was reported.[4] The structure consists of isolated $[VF_4(OH_2)_2]^-$ octahedra and ten-co-ordinate Rb^+ cations.

EXPERIMENTAL

Preparation.—Manganese(III) oxide (0.01 mol), prepared as described elsewhere,[5] was dissolved in 20% hydrofluoric acid (10 cm³; Riedel, AnalaR). A solution of CsF (0.01 mol; Alfa Inorganics, AnalaR) in 20% HF (10 cm³) was added and the solution was allowed to stand at room temperature overnight. The resulting brown-violet *crystals* were filtered off, washed with methanol, and dried *in vacuo* {Found: Cs, 43.9; F, 25.6; Mn, 18.45. $Cs[MnF_4(OH_2)_2]$ requires Cs, 44.3; F, 25.35; Mn, 18.3; H_2O, 12.0%}. The preparation was repeated with Cs : Mn mol ratios of 2, 5, 10, and 20 : 1 respectively. Increasing the amount of CsF resulted in ready precipitation of the required complex. Crystals suitable for X-ray structural analysis were therefore obtained by slow evaporation of the solution containing the smallest Cs : Mn ratio.

The deuteriated analogue was prepared by carrying out the synthesis in deuterium oxide (B.D.H.; minimum isotopic purity, 99.7%) acidified with deuterium fluoride. Recrystallization of $Cs[MnF_4(OH_2)_2]$ from D_2O was impossible due to strong hydrolysis.

Physical Measurements.—Infrared spectra were recorded in Nujol mulls between potassium bromide plates on a Perkin-Elmer 521 instrument in the 250—4 000 cm⁻¹ region. Magnetic-susceptibility measurements were made on a Gouy balance. They confirmed a d^4 high-spin state for the manganese ($\mu_{eff.}$ 5.0 B.M.).[‡]

Crystal Data.—$H_4CsF_4MnO_2$, $M = 299.88$, Monoclinic, $a = 11.907(2)$, $b = 6.597(1)$, $c = 9.316(2)$ Å, $\beta = 121.77(1)°$, $U = 622.16$ Å³, D_m (by flotation) $= 3.19(3)$ g cm⁻³ $Z = 4$, $D_c = 3.200$ g cm⁻³, $F(000) = 544$, $\mu(\text{Mo-}K_\alpha) = 80.8$ cm⁻¹. Space group $C2/c$–C^6_{2h}.

Preliminary cell dimensions and space-group symmetry were determined from rotation and Weissenberg photographs (Cu-K_α radiation). Accurate cell parameters were obtained from a least-squares fit of the 2θ values of 27 reflections from $h0l$ and $0kl$ Weissenberg photographs calibrated with superimposed aluminium ($a_0 = 4.049\,07$ Å) powder lines, using Cu-$K_{\alpha 1}$ radiation at 20(1) °C.

Three-dimensional intensity data were collected on an Enraf–Nonius CAD-4 automatic diffractometer with ω—2θ scan and graphite-monochromated Mo-K_α radiation. A crystal of dimensions $0.28 \times 0.18 \times 0.14$ mm was used. The whole sphere of reflections (3 796 in all) in the range $1.5 < \theta < 30.0°$ was measured. The symmetry-related reflections were averaged (mean discrepancy on $I = 7.1\%$) to yield 907 independent reflections of which 835 with $I_0 > 3\sigma(I_0)$ (obtained from counting statistics) were considered observed and used for the structure analysis. Lorentz-polarization corrections were applied, but no absorption corrections were made (μR *ca.* 0.8).

Structure Determination and Refinement.—The position of the caesium atom was obtained from a three-dimensional Patterson map, while the subsequent electron-density map gave co-ordinates for all the non-hydrogen atoms. After three cycles of full-matrix least-squares refinement with anisotropic temperature factors for all the atoms, R was 0.066. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weighting function $w = W_FW_S$ was determined empirically from $W_F(|F_o| < 25.0) = (|F_o|/25.0)^{1.5}$, $W_F(|F_o| > 65.0) = (65.0/|F_o|)^3$, and $W_F(25.0 < |F_o| < 65.0) = 1.0$, and $W_S(\sin\theta < 0.42) = (\sin\theta/0.42)^3$, $W_S(\sin\theta > 0.50) = (0.50/\sin\theta)^{1.5}$, and $W_S(0.42 < \sin\theta < 0.50) = 1.0$. The difference electron-density map revealed the positions of the hydrogen atoms. These atoms were included in the refinement as invariants with isotropic thermal parameters $U = 0.06$ Å². Refinement terminated at R 0.024 ($= \Sigma|\Delta F|/|F_o|$) and R' 0.022 $\{= [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$. An extinction parameter [6] was included in the refinement and its final value was 3.388×10^{-3}. Atomic scattering factors for H atoms were taken from ref. 7 and for other atoms from ref. 8, those for Cs, Mn, F, and O being corrected for the effects of anomalous scattering ($\Delta f'$, $\Delta f''$).[9]

[†] Presented in part at the 2nd Yugoslav–Italian Crystallographic Conference, Dubrovnik, June 1976.

[‡] Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m².

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All the calculations were made on the CDC CYBER 72 computer at RRC Ljubljana using the '*X*-Ray '72' system of crystallographic programs.[10]

Final structure factors are listed in Supplementary Publication No. SUP 21999 (6 pp., 1 microfiche).*

RESULTS AND DISCUSSION

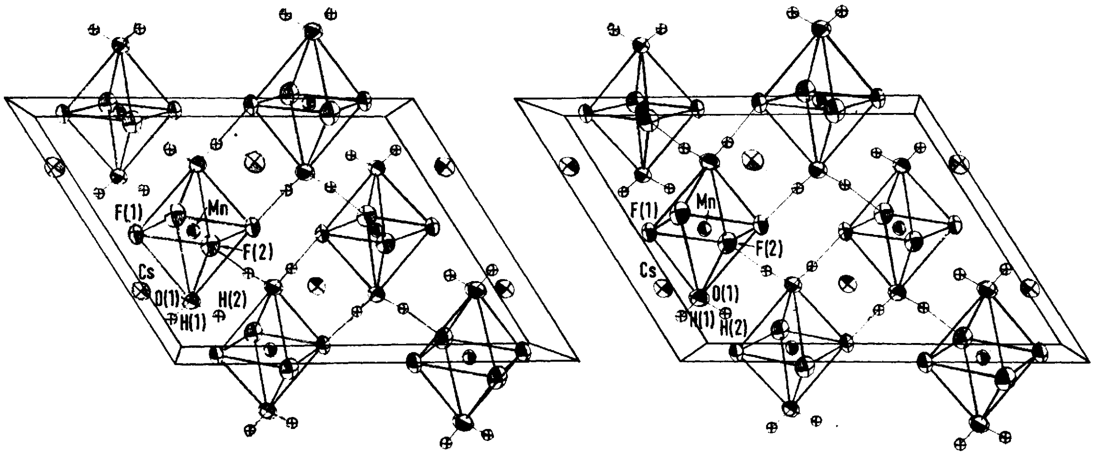
The final atomic positional and thermal parameters are presented in Table 1, while interatomic distances and angles are listed in Table 2. A stereoscopic view of the unit cell down the *b* axis and the atom numbering are shown in the Figure. The structure contains separate $[MnF_4(OH_2)_2]^-$ anions, interlinked by a net of hydrogen bonds of the type $O-H \cdots F$, extending throughout the unit cell. Mn–F and Mn–O bond lengths clearly indicate tetragonal elongation of the manganese octahedron. A number of metal–ligand bond distances in octahedral high-spin manganese(III) complexes, tabulated by Stults *et al.*,[11] can be compared with our results. The Jahn–Teller distortion in $Cs[MnF_4(OH_2)_2]$ is of the same type as in hexa- and penta-fluoromanganates(III) with short Mn–F bonds (1.83—1.92 Å) and long *trans* Mn–F bonds (2.06—2.09 Å). The corresponding values for the Mn–O distances in several homo- and hetero-ligand species are 1.89—1.96 and 2.11—2.33 Å respectively. It is also interesting to mention the data of the isostructural $Rb[VF_4(OH_2)_2]$ (V–F 1.90, 1.91; V–O 2.07 Å).[4] The differences in bond lengths between the vanadium and manganese complexes confirm the expected strong Jahn–Teller effect in weak-field d^4 complexes. The caesium atom is bound to eight fluorine and two oxygen atoms (see Table 2).

TABLE 1

Final fractional co-ordinates ($\times 10^5$ for non-hydrogen atoms, $\times 10^4$ for hydrogen atoms) and thermal parameters[a] with estimated standard deviations in parentheses

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	0	72 143(4)	25 000	265(2)	242(2)	299(2)		117(1)	
Mn	25 000	25 000	50 000	140(2)	201(3)	189(2)	−5(1)	88(2)	24(1)
F(1)	9 581(15)	32 805(28)	48 632(22)	182(6)	381(8)	321(7)	12(5)	142(6)	−17(6)
F(2)	26 862(20)	50 986(27)	44 163(26)	360(9)	256(7)	419(9)	−15(6)	233(8)	88(6)
O(1)	13 299(21)	15 238(41)	23 312(26)	244(9)	541(13)	221(8)	99(8)	91(7)	−41(8)
H(1)[b]	524	2 129	1 591						
H(2)	1 789	1 031	1 754						

[a] The anisotropic thermal factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^4]$. [b] See text.



Projection of the structure down the *b* axis and numbering of the atoms

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances and angles of Mn octahedron			
Mn–F(1)	1.846(2)	F(1)–Mn–F(2)	89.4(1)
Mn–F(2)	1.847(2)	F(1)–Mn–O(1)	89.3(1)
Mn–O(1)	2.211(2)	F(2)–Mn–O(1)	92.4(1)
(*b*) Hydrogen bonds			
O(1)–H(1)–$F(1^{I})$	2.661(3)	O(1)–H(2)–$F(2^{II})$	2.630(4)
(*c*) Distances of Cs polyhedron			
Cs–F(1),$F(1^{I})$	3.200(2)	Cs–$F(2^{V})$,$F(2^{VI})$	3.264(2)
Cs–$F(1^{III})$,$F(1^{IV})$	3.224(2)	Cs–$O(1^{VII})$,$O(1^{VIII})$	3.298(3)
Cs–F(2),$F(2^{I})$	3.058(2)		

Roman numeral superscripts refer to the following co-ordinate transformations:

I $-x, y, \frac{1}{2} - z$	V $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$
II $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	VI $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$
III $-x, 1 - y, 1 - z$	VII $x, 1 + y, z$
IV $x, 1 - y, -\frac{1}{2} + z$	VIII $-x, 1 + y, \frac{1}{2} - z$

The i.r. bands of the present complex and of its deuteriated analogue are given in Table 3. The observed internal vibrations of the anion can be explained

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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by the site-group approach. Considering only i.r.-active modes, the correlation gives:

$$\begin{array}{c} D_{4h} \qquad\qquad C_i \\ 2A_{2u} + B_{2u} + 3E_u \rightarrow 9A_u \end{array}$$

There should be no coincidences between the i.r. and Raman spectra as the centre of symmetry is preserved in the solid. There were two i.r.-active Mn–F stretching modes, as predicted by C_i site symmetry, occurring in the region already known for six-co-ordinate fluorometallates.[12-14] Both frequencies lie much closer than, for instance, in $K_2[MnF_5]\cdot H_2O$ (580, 480, and 410 cm^{-1})[14] where the fluorides act as terminal and bridging ligands.

TABLE 3

Infrared bands in the range 250—4 000 cm^{-1}

Assignment	$Cs[MnF_4(OH_2)_2]$	$Cs[MnF_4(OD_2)_2]$
ν(OH)	3 450vs	2 490vs
	3 310m (sh)	2 385s
δ(HOH)	1 665m	1 217m
lib(H_2O)	730m (sh)	525m (sh)
	665s	470m
ν(MnF)	590vs (sh)	585vs
	560vs	560vs
ν(Mn–O)	370w	367w
δ(FMnF)	276s	275s
	260s	260s

The band at 370 cm^{-1} showed a slight bathochromic shift on deuteriation and has been assigned to ν(Mn–OH_2). Adams and Lock[15] found the i.r.-active Mn–OH_2 stretching in rubidium and caesium salts of *trans*-$[MnCl_4(OH_2)_2]^{2-}$ at 337 and 295 cm^{-1}, respectively. The main difference between our complex and both chloromanganates is the higher oxidation state in our case, causing the Mn–OH_2 stretching to appear at a higher frequency.

The remaining two bands in the low-frequency region may be associated with the FMnF deformation modes. In addition, there should be four deformation modes involving fluorine and oxygen atoms, which were not observed above 250 cm^{-1}. The two bands below 800 cm^{-1}, which shifted considerably on deuteriation, belong to librations of the co-ordinated water molecules. Most workers have assigned the higher frequency to rocking and the lower one to the wagging mode. Adams and Lock,[15] on the other hand, employed arguments (sensitivity to change of cation) for the reverse assignment in some aquahalogeno-complexes. In the case of Cs-$[MnF_4(OH_2)_2]$, hydrogen bonds affect all the external vibrational motions of water and the distinction between wag and rock can only be tentative.

[6/1989 *Received, 26th October*, 1976]

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