Syntheses and Crystal Structures of Tetramethylammonium Diaquatetrafluoromanganate(III) and Rubidium Aquatetrafluoromanganate(III)

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The crystal structures of the title complexes, $[NMe_4][MnF_4(OH_2)_2]$ (1) and $Rb[MnF_4(OH_2)]$ (2), have been determined by three-dimensional Patterson–Fourier and least-squares methods based on *X*-ray (Mo-K_α) diffraction data. Complex (1) has been isolated from an aqueous solution of the corresponding fluorides. It crystallizes in space group *C*2/*c* with a = 16.092(3), b = 5.559(1), c = 10.844(2) Å, β = 97.59(2)°, Z = 4, and R = 0.033. The structure consists of $[MnF_4(OH_2)_2]^-$ anions, which are tetragonally elongated octahedra, linked by hydrogen bonds to form layers parallel to *x*00 planes with tetramethylammonium cations between the layers. Complex (2) crystallizes from acid solution as monoclinic crystals of space group *C*2/*c* with a = 13.932(2), b = 6.471(1), c = 10.635(1) Å, β = 105.54(1)°, Z = 8, and R = 0.037. The structure consists of $[MnF_6]^{3-}$ and $[MnF_4(OH_2)_2]^-$ octahedra alternating in the *ac* direction. Rubidium cations as well as hydrogen bonds bind the anion chains together. The observed distortion of the octahedra in both structures is ascribed to the Jahn–Teller effect.

As a part of our study on fluorometallates(III) we previously reported the synthesis and crystal structure of $Cs[MnF_4(OH_2)_2]$.[1] The complex consists of $[MnF_4(OH_2)_2]^-$ octahedra interlinked by a three-dimensional array of hydrogen bonds. The octahedral anions are tetragonally elongated due to the Jahn–Teller effect. A similar situation is now found in the complex $[NMe_4][MnF_4(OH_2)_2]$ (1), together with the effect of cation size on the structure.

In the case of rubidium, there has only been a short note on the preparation of $Rb_3[MnF_6]$,[2] and recently we reported [3] the crystal structure of $Rb_2[MnF_5]\cdot H_2O$ in which $[MnF_6]^{3-}$ octahedra are linked through *trans*-bridging fluorine atoms to give infinite kinked chains of composition $[MnF_5]_n^{2n-}$. The complex $Rb[MnF_4(OH_2)]$ (2) contains $[MnF_6]^{3-}$ and $[MnF_4(OH_2)_2]^-$ octahedra to form infinite chains of composition $[MnF_4(OH_2)]^-$.

In this paper we report the syntheses and crystal structures of complexes (1) and (2).

EXPERIMENTAL

Preparations.—The complexes were prepared analogously to caesium tetrafluoromanganate(III).[1] Crystallizations of (1) were performed in 4, 10, and 20% hydrofluoric acid with NMe_4 : Mn mol ratios of 1, 3, 5, and 10 : 1 respectively. From the *X*-ray powder photographs, it was evident that the same *compound* was formed in all cases {Found: F, 31.2; Mn, 22.6; NMe_4, 30.35; H_2O, 15.25. $[NMe_4][MnF_4(OH_2)_2]$ requires F, 31.5; Mn, 22.8; NMe_4, 30.75; H_2O, 14.95%}. For (2), manganese(III) oxide (0.01 mol) was dissolved in 20% hydrofluoric acid (10 cm³), and a solution of RbF (0.01 mol in 10 cm³ of 20% HF) was added. After several hours, brown-violet *crystals* formed, which were filtered off, washed with methanol, and dried *in vacuo* {Found: F, 32.6; Mn, 23.3; Rb, 36.2; H_2O, 7.65. $Rb[MnF_4(OH_2)]$ requires F, 32.4; Mn, 23.45; Rb, 36.45; H_2O, 7.70%}.

Magnetic Susceptibility.—Measurements made on a Gouy balance showed a d^4 high-spin state for the manganese in both complexes: $\mu_{\text{eff.}}$ = 4.90 for (1) and 4.70 B.M. for (2) at 20 °C. Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m².

X-Ray Analysis.—Crystals of (1) were unstable in air and the crystal of dimensions 0.28 × 0.30 × 0.40 mm used for data collection was mounted in a Lindemann glass capillary, while crystals of (2) were stable in air and the crystal (0.16 × 0.22 × 0.28 mm) used for data collection was mounted on a glass thread. The densities were determined by the flotation method. The crystal data are listed in Table 1. For both complexes, preliminary cell dimensions and space-group symmetry were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation. Accurate cell parameters were obtained by least-squares treatment of 30 high-angle reflections, collected on an Enraf–Nonius CAD-4 automatic diffractometer, using nickel-filtered Cu-K_α radiation. Intensity data were recorded with the ω—2θ scan technique in the interval $1.5 < \theta < 75.0°$. For each complex, three standard reflections were measured at intervals of 100 reflections; no variation of their intensity was observed.

TABLE 1

Crystal data

	Complex	
Parameter	(1)	(2)
Molecular formula	$C_4H_{16}F_4MnNO_2$	H_2F_4MnORb
Formula weight	241.15	234.43
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)
a/Å	16.092(3)	13.932(2)
b/Å	5.559(1)	6.471(1)
c/Å	10.844(2)	10.635(1)
β/°	97.59(2)	104.54(1)
U/Å³	961.6	928.1
D_m/g cm⁻³	1.67(3)	3.30(5)
D_c/g cm⁻³	1.665	3.354
Z	4	8
F(000)	496	864
λ/Å	1.5418	1.5418
μ/cm⁻¹	121.7	387.4
Number of unique intensities collected	990	957
Number of intensities with $I > 3\sigma(I)$	740	817

The data for both complexes were corrected for Lorentz and polarization effects. An absorption correction was applied for (2).

Structure Analyses.—For (1), the position of the manganese atom was determined from a three-dimensional Patterson map. Positions for the other non-hydrogen atoms were established from F_o Fourier synthesis. Atomic positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to R 0.046. The function minimized was $\Sigma w|\Delta F|^2$, where the weighting function w was determined empirically (Table 2). The positions of the hydrogen atoms were obtained from a difference-Fourier synthesis and were included in the least-squares refinement as invariants with isotropic thermal parameters $U = 0.06$ Å^2. This final refinement converged at R 0.033 ($=\Sigma|\Delta F|/|F_o|$), and R' 0.031 $\{ = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$.

For (2), a three-dimensional E map yielded co-ordinates for the rubidium and for both manganese atoms. The sites of the remaining atoms other than hydrogen were established from a three-dimensional F_o Fourier synthesis phased by the rubidium and the manganese atoms. Atomic positional and isotropic thermal parameters were then refined by full-matrix least-squares analysis to R 0.087. Three cycles of least-squares refinement, with anisotropic temperature factors for all atoms, reduced R to 0.059. Attempts to locate the hydrogen atoms from a difference electron-density map were unsuccessful. An extinction parameter[4] (final value 2.01×10^{-3}) was included in further refinement which converged, after six cycles of full-matrix least-squares calculations, at R 0.037, R' 0.027. The same function was minimized as in the case of (1), the weighting function used being presented in Table 2.

TABLE 2

Weighting functions

Parameter	Complex (1)	Complex (2)
A	25.0	80.0
B	40.0	120.0
C	2.0	2.0
D	2.0	3.0
E	0.70	0.70
G	0.85	0.85
H	2.0	3.0
J	2.0	2.0

$F_o < A$, $W_F = (F_o/A)^D$ $\quad$ $\sin\theta < E$, $W_S = (\sin\theta/E)^H$

$A \leqslant F_o \leqslant B$, $W_F = 1.0$ $\quad$ $E \leqslant \sin\theta \leqslant G$, $W_S = 1.0$

$F_o > B$, $W_F = (B/F_o)^D$ $\quad$ $\sin\theta > G$, $W_S = (G/\sin\theta)^J$

$w = W_F W_S$

The atomic scattering factors for H atoms were taken from ref. 5 and for the other atoms from ref. 6, with those of non-hydrogen atoms corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 7. All the calculations were carried out on the CDC CYBER 72 computer at RRC Ljubljana using the MULTAN and 'X-Ray '72' systems of crystallographic programs.[8,9] Table 3 shows positional parameters for (1) and (2) respectively. Final structure factors and temperature factors are listed in Supplementary Publication No. SUP 22567 (13 pp.).*

RESULTS AND DISCUSSION

$[NMe_4][MnF_4(OH_2)_2]$ (1).—Interatomic distances and angles are given in Table 4. The structure, illustrated in Figure 1, consists of discrete $[MnF_4(OH_2)_2]^-$ anions and $[NMe_4]^+$ cations. The Mn–O and the two Mn–F bond lengths show tetragonal elongation of the octahedron as expected for high-spin manganese(III) complexes. There is also a difference of 0.06 Å between the two equatorial Mn–F bond distances. It arises because the F(2) fluorine atom forms two hydrogen bonds to the adjacent water molecules, whereas the F(1) fluorine atom does not take part in hydrogen bonding. Thus layers are formed in the x00 planes with x 0.25 and 0.75 (Figure 2). Both hydrogen atoms of the water molecule were placed at 0.98 Å from the oxygen, with an angle of 104.4° between them.

TABLE 3

Final fractional co-ordinates (×10^5 for non-hydrogen atoms, ×10^4 for hydrogen atoms) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
(a) For (1)			
Mn	25 000	25 000	50 000
F(1)	14 018(8)	28 594(33)	44 133(15)
F(2)	25 824(10)	460(27)	38 473(14)
O(1)	28 677(15)	52 739(35)	36 477(18)
N(1)	50 000	15 500(60)	25 000
C(1)	44 217(26)	30 766(65)	16 414(50)
C(2)	45 103(19)	−364(74)	32 470(30)
H(1)	2 659	5 287	2 761
H(2)	2 902	6 971	3 881
H(3)	4 059	2 115	916
H(4)	4 004	3 980	2 168
H(5)	4 784	4 380	1 229
H(6)	4 144	−1 145	2 593
H(7)	4 917	−1 096	3 879
H(8)	4 118	1 009	3 754
(b) For (2)			
Rb	7 960(3)	74 353(18)	43 814(5)
Mn(1)	25 000	25 000	50 000
Mn(2)	0	24 661(42)	25 000
F(1)	10 764(17)	25 284(134)	43 540(25)
F(2)	25 085(28)	−1 929(58)	45 722(39)
F(3)	6 721(53)	4 281(86)	18 496(71)
F(4)	6 936(47)	44 697(86)	18 997(67)
O(1)	26 498(31)	33 599(85)	30 934(44)

The tetramethylammonium cations are located between the layers with nitrogen atoms on the two-fold symmetry axes. The interatomic distances and angles in the tetramethylammonium group are close to the reported values.[10] The shortest distance between carbon and fluorine is 3.120(4) Å. This is slightly less than the sum of van der Waals radii for carbon and fluorine,[11] 3.15 Å, which can be an indication of hydrogen bonding between cations and anions.[12]

It is interesting to compare the crystal structure of $[NMe_4][MnF_4(OH_2)_2]$ to that of $Cs[MnF_4(OH_2)_2]$,[1] because the effect of the cation size can be seen. By replacing $[NMe_4]^+$ with the smaller Cs^+ cation, the anionic layers come closer together, whereas the a axis reduces from 16.092(3) to 11.907(2) Å. The closer

TABLE 4

Bond lengths (Å) and angles (°) in (1), with estimated standard deviations in parentheses

(a) Distances and angles of Mn octahedron			
Mn–F(1)	1.808(1)	F(1)–Mn–F(2)	89.9(1)
Mn–F(2)	1.867(2)	F(1)–Mn–O(1)	91.4(1)
Mn–O(1)	2.260(2)	F(2)–Mn–O(1)	90.0(1)
(b) Distances and angles of tetramethylammonium ion			
N(1)–C(1)	1.491(5)	C(1)–N(1)–C(2)	110.2(2)
N(1)–C(2)	1.491(4)	C(1)–N(1)–C(1^{I})	110.6(3)
		C(1)–N(1)–C(2^{I})	109.2(2)
		C(2)–N(1)–C(2^{I})	107.5(3)
(c) Hydrogen bonds			
O(1)–H(1) · · · F(2^{II})	2.710(2)		
O(1)–H(2) · · · F(2^{III})	2.706(2)		

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

I $1 - x, y, \frac{1}{2} - z$

II $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

III $x, 1 + y, z$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

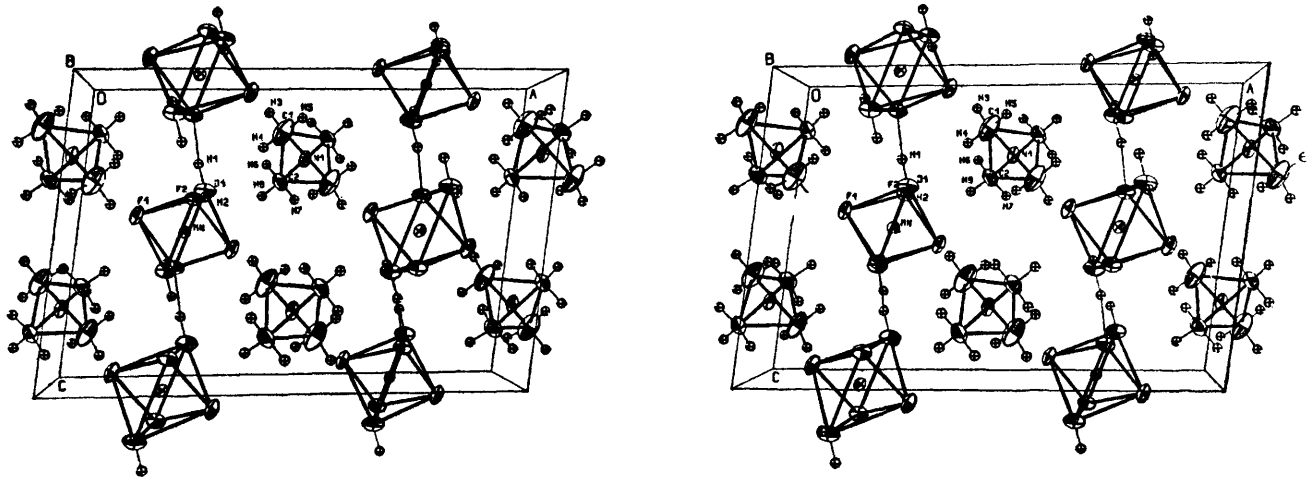

FIGURE 1 Stereoscopic view of complex (1) down the *b* axis and numbering of the atoms

layers and reorientated octahedra in (1) now allow both crystallographically non-equivalent fluorine atoms to form hydrogen bonds, which interlink the $[MnF_4(OH_2)_2]^-$ anions in three dimensions.

$Rb[MnF_4(OH_2)]$ (2).—Interatomic distances and angles are given in Table 5. The structure, shown in Figure 3, consists of endless-chain anions aligned along the *ac* direction, and rubidium cations placed between them on general eight-fold positions. The chains are formed of alternating $[MnF_6]^{3-}$ and $[MnF_4(OH_2)_2]^-$ octahedra, interlinked through *trans*-fluorine atoms.

The $[MnF_4(OH_2)_2]^-$ anion, with a manganese atom at the inversion centre, is elongated in the oxygen direction due to the Jahn–Teller effect. The Mn–O bond length of 2.163(5) Å is characteristic for 'long' axial Mn–O distances of high-spin manganese(III) compounds. The two 'short' equatorial Mn–F bond lengths are also close to the reported values.[13] The $[MnF_4(OH_2)_2]^-$

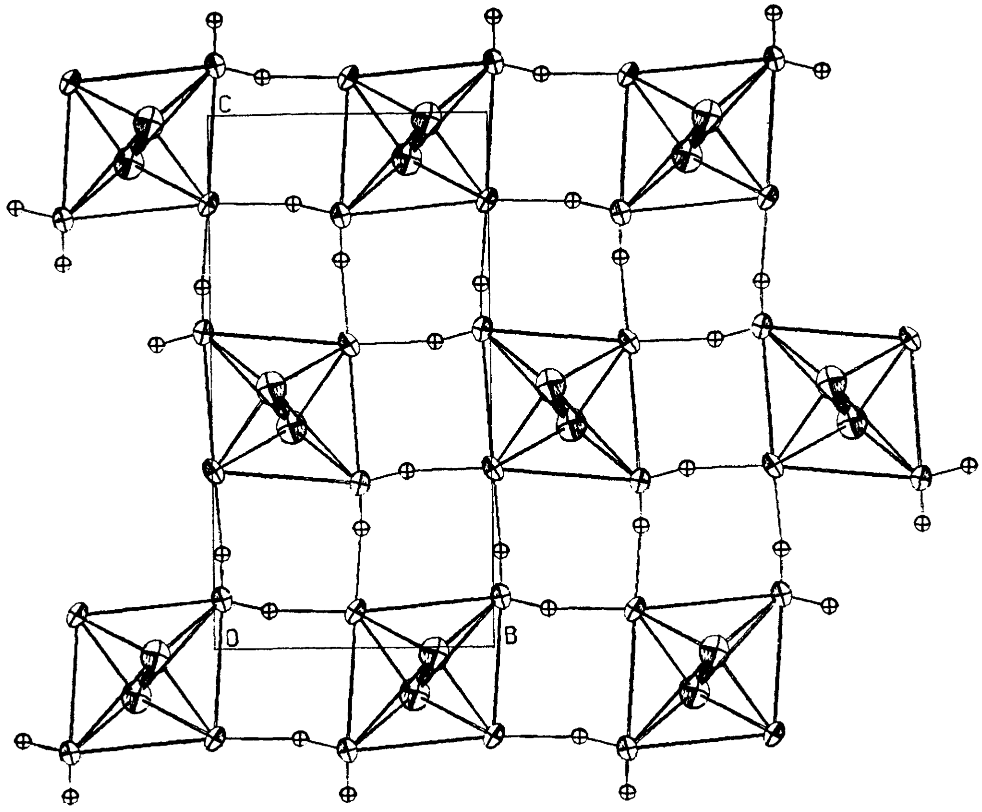

FIGURE 2 Projection of complex (1) down the *a* axis

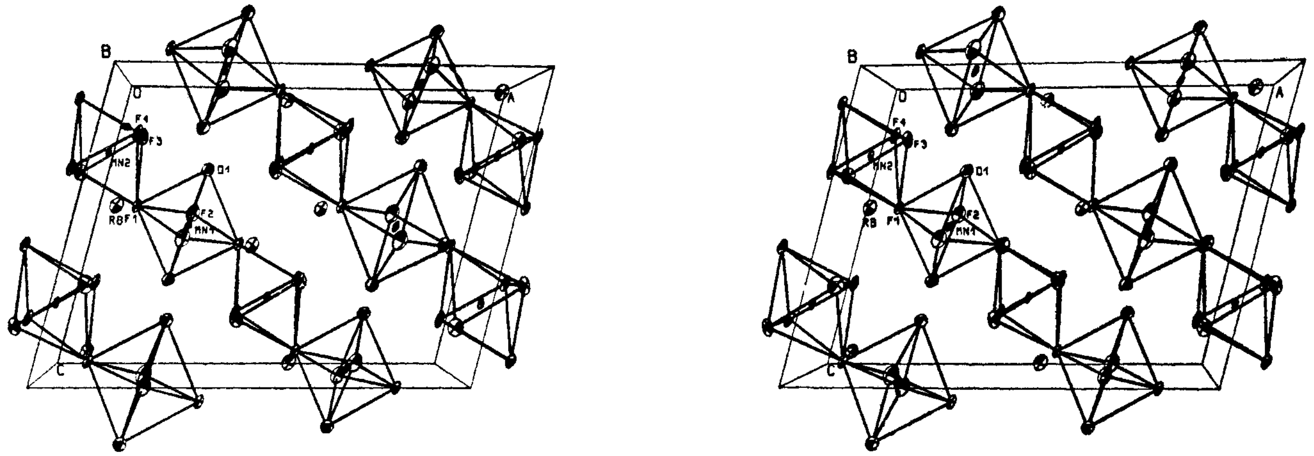

FIGURE 3 Stereoscopic view of complex (2) down the *b* axis and numbering of the atoms

octahedra share their F(1) fluorine atoms. As a consequence, the electron density between Mn and F(1) is lowered, which results in a lengthening of the Mn–F(1) bond distance.

The $[\mathrm{MnF_6}]^{3-}$ octahedra are placed on two-fold symmetry axes and are tetragonally elongated in the direction of the bridging fluorine atoms. The two equatorial Mn–F distances are nearly the same, whereas the axial bond length of 2.157(2) Å represents the longest Mn–F distance known. A minor part of the elongation may be due to sharing of fluorine atoms, but the principal part is to be ascribed to the operation of the Jahn–Teller effect.

TABLE 5

Bond lengths (Å) and angles (°) in (2), with estimated standard deviations in parentheses

(*a*) Distances and angles of Mn(1) octahedron

Mn(1)–F(1)	1.929(2)	F(1)–Mn(1)–F(2)	89.5(3)
Mn(1)–F(2)	1.802(4)	F(1)–Mn(1)–O(1)	89.8(1)
Mn(1)–O(1)	2.163(5)	F(2)–Mn(1)–O(1)	90.2(2)

(*b*) Distances and angles of Mn(2) octahedron

Mn(2)–F(1)	2.157(2)	F(1)–Mn(2)–F(3)	93.1(3)
Mn(2)–F(3)	1.849(7)	F(1)–Mn(2)–F(4)	89.9(3)
Mn(2)–F(4)	1.825(7)	F(1)–Mn(2)–F(3^{I})	88.4(3)
		F(1)–Mn(2)–F(4^{I})	88.5(3)
		F(3)–Mn(2)–F(4)	90.8(3)
		F(3)–Mn(2)–F(3^{I})	89.0(3)
		F(4)–Mn(2)–F(4^{I})	89.5(3)
		F(1)–Mn(2)–F(1^{I})	117.8(4)
		F(3)–Mn(2)–F(4^{I})	178.3(3)

(*c*) Distances of Rb polyhedron

Rb–F(1)	3.200(9)	Rb–F(3^{III})	3.286(7)
Rb–F(4)	3.237(7)	Rb–F(1^{IV})	3.221(3)
Rb–F(4^{I})	2.903(6)	Rb–F(2^{V})	2.758(4)
Rb–F(1^{III})	3.320(9)	Rb–F(3^{VI})	3.010(8)
Rb–F(2^{III})	2.801(4)	Rb–F(3^{VII})	2.882(6)
		Rb–F(4^{VI})	2.984(7)

(*d*) Hydrogen bonds

interchain		intrachain	
O(1) · · · F(2^{II})	2.941(6)	O(1) · · · F(4)	2.796(7)
O(1) · · · F(3^{II})	2.681(8)		

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

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

The F(2) and F(3) fluorine atoms are involved in interchain, and F(4) fluorine atom in intrachain, hydrogen bonding (see Table 5).

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