SHORT-FORMAT PAPERS

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Chain Structure of K[MnF₄(H₂O)]

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Abstract. K[MnF$_4$(H$_2$O)], $M_r = 188 \cdot 1$, monoclinic, $C2/c$, $a = 13 \cdot 891$ (2), $b = 6 \cdot 212$ (1), $c = 10 \cdot 484$ (2) Å, $\beta = 104 \cdot 74$ (2)°, $V = 874 \cdot 9$ Å^3, $Z = 8$, $D_x = 2 \cdot 855$ g cm^{-3}, λ(Mo $K\alpha$) = 0 $\cdot$ 7107 Å, $\mu = 37 \cdot 6$ cm^{-1}, $F(000) = 720$, $T = 295$ (1) K, $R = 0 \cdot 042$ for 833 observed reflections. Crystals were grown by reducing an aqueous hydrofluoric acid solution of KMnO$_4$ with acetylacetone. The structure is isotypic with Rb[MnF$_4$(H$_2$O)] and consists of parallel chains formed by alternating [MnF$_6$] and [Mn(H$_2$O)$_2$F$_4$] octahedra sharing *trans* fluoride ligands. Both types of octahedra exhibit strong Jahn–Teller distortions and show antiferrodistortive ordering along the chain direction.

Experimental. Brown crystals of K[MnF$_4$(H$_2$O)] were prepared by adding acetylacetone to a solution of 1·5 g KMnO$_4$ in 10% aqueous hydrofluoric acid until the permanganate colour disappeared. The analogous Rb compound has been prepared previously by Kaučič & Bukovec (1979) using a different method. The compounds are of interest owing to their one-dimensional magnetic properties. Transparent brown coffin-lid-shaped crystals, 0·26 × 0·20 × 0·10 mm, CAD-4 diffractometer (Enraf–Nonius), Mo $K\alpha$ radiation, graphite monochromator, cell parameters from least-squares fit of 25 high-angle reflections

$(10 < \theta < 25°)$. ω-scanning mode over $(1 \cdot 0 + 0 \cdot 35 \tan\theta)°$ and, in addition, 25% before and after each reflection for background determination; maximum measuring time 30 s per reflection, measuring range $1 \le \theta \le 30°$, $h -19/18$, k 0/8, l 0/14; two intensity control reflections measured every hour, maximum deviation 4%. Total of 1347 reflections, after averaging ($R_{int} = 0 \cdot 022$) 1280 unique reflections, 833 with $F_o > 3\sigma$; no correction for absorption or extinction. Systematic absences conform to space group Cc and $C2/c$. The latter has been chosen by analogy with the corresponding Rb compound (Kaučič & Bukovec, 1979). There was no evidence for any deviation from centrosymmetry. Refinement starting from the atomic parameter set of the Rb compound by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976), function minimized $w(|\,|F_o| - |F_c|\,|)^2$. H atoms located

Table 1. *Atomic fractional coordinates and equivalent isotropic temperature factors* (Å^2)

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

	x	y	z	U_{eq}
Mn(1)	0·2500	0·2500	0·5000	0·0136 (3)
Mn(2)	0·0000	0·2471 (3)	0·2500	0·0130 (3)
K	0·0806 (1)	0·7422 (3)	0·4427 (1)	0·0294 (5)
F(1)	0·1079 (2)	0·2544 (7)	0·4362 (2)	0·0160 (11)
F(2)	0·2503 (3)	−0·0315 (4)	0·4621 (3)	0·0276 (15)
F(3)	0·0648 (3)	0·0351 (6)	0·1822 (4)	0·0323 (23)
F(4)	0·0675 (3)	0·4560 (6)	0·1859 (4)	0·0323 (23)
O	0·2648 (3)	0·3251 (7)	0·3058 (4)	0·0266 (17)
H(1)	0·222 (7)	0·398 (14)	0·262 (9)	0·06 (3)
H(2)	0·307 (7)	0·427 (16)	0·320 (9)	0·07 (3)

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Mn(1)–F(1)	1·916 (2)	F(1)–Mn(1)–F(2)	89·8 (2)
Mn(1)–F(2)	1·794 (3)	F(1)–Mn(1)–O	90·3 (1)
Mn(1)–O	2·149 (4)	F(2)–Mn(1)–O	89·7 (1)
Mn(2)–F(1)	2·138 (2)	F(1)–Mn(2)–F(1^{vi})	177·5 (1)
Mn(2)–F(3)	1·837 (4)	F(1)–Mn(2)–F(3)	94·0 (2)
Mn(2)–F(4)	1·826 (4)	F(1)–Mn(2)–F(3^{vi})	87·8 (2)
		F(1)–Mn(2)–F(4)	90·8 (2)
K–F(1)	3·057 (5)	F(3)–Mn(2)–F(3^{vi})	88·4 (2)
K–F(1^i)	3·205 (5)	F(3)–Mn(2)–F(4)	91·1 (1)
K–F(1^{ii})	3·187 (5)	F(3)–Mn(2)–F(4^{vi})	180·0 (1)
K–F(2^i)	2·708 (3)	F(4)–Mn(2)–F(4^{vi})	89·4 (1)
K–F(2^{iii})	2·653 (3)	Mn(1)–F(1)–Mn(2)	137·7 (1)
K–F(3^i)	3·242 (4)		
K–F(3^{iv})	2·924 (4)	Hydrogen bonds	
K–F(3^v)	2·785 (4)	Intrachain	
K–F(4)	3·192 (4)	O$\cdots$F(4)	2·829 (8)
K–F(4^{iv})	2·879 (4)	O–H(1)$\cdots$F(4)	149 (7)
K–F(4^{vi})	2·792 (4)		
		Interchain	
K–F mean	2·966	O$\cdots$F(3^{vii})	2·678 (8)
		O–H(2)$\cdots$F(3^{viii})	148 (7)

Symmetry operations: (i) x, 1 + y, z; (ii) $-x$, 1 − y, 1 − z; (iii) $\tfrac{1}{2}$ − x, $\tfrac{1}{2}$ − y, 1 − z; (iv) x, 1 − y, $\tfrac{1}{2}$ + z; (v) $-x$, 1 + y, $\tfrac{1}{2}$ − z; (vi) − x, y, $\tfrac{1}{2}$ − z; (vii) $\tfrac{1}{2}$ −x, $\tfrac{1}{2}$ + y, $\tfrac{1}{2}$ − z.
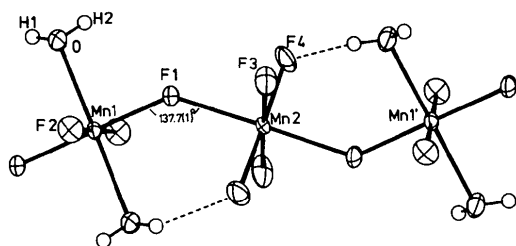
Fig. 1. ORTEP (Johnson, 1965) drawing of a section of the linear-chain anion with thermal ellipsoids at the 50% probability level. Mn(1) lies on a inversion center, Mn(2) on a twofold axis approximately perpendicular to the plane of the drawing.

by difference Fourier synthesis and included in the refinement with isotropic temperature factors. Anisotropic temperature factors used for the heavier atoms. Atomic scattering factors for neutral atoms from Cromer & Mann (1968), corrections for anomalous dispersion from Cromer & Liberman (1970). Final $R = 0.042$, $wR = 0.036$ with weights $w = 1/\sigma^2(F_o)$ for the 833 observed reflections.* $(\Delta/\sigma)_{max} = 0.005$, $\Delta\rho_{max,min} = 0.33$, -0.35 e Å^{-3}. The final atomic parameters are given in Table 1, and interatomic distances and angles are given in Table 2. Fig. 1 shows a section of the infinite linear-chain anions, Fig. 2 the orientation of the chains in the cell and the positions of the K cations.

Related literature. The isotypic structure of Rb[MnF$_4$(H$_2$O)] was determined by Kaučič & Bukovec (1979). Magnetic studies on the Rb and K compounds have been published by Massa & Pebler (1986), Palacio, Andres, Horne & van Duynefeldt (1986), Nuñez, Darriet, Bukovec, Tressaud & Hagenmuller (1987) and Pebler, Massa, Lass & Ziegler (1987).

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44397 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
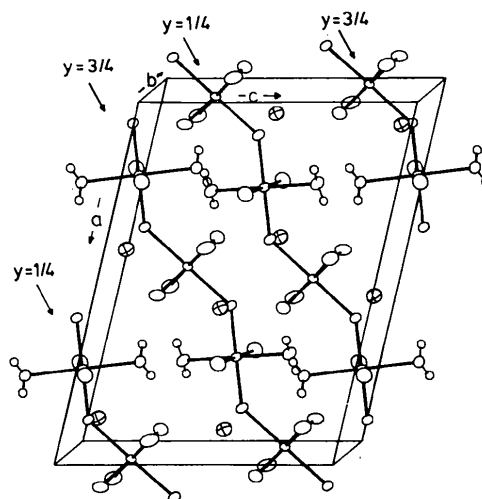

Fig. 2. View of the unit-cell contents illustrating the chain packing.

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Structure of a New Polymorph of Bis(μ-pyridine N-oxide)-bis[aquadichlorocopper(II)]

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Abstract. [Cu$_2$Cl$_4$(H$_2$O)$_2$(C$_5$H$_5$NO)$_2$], $M_r = 495.14$, monoclinic, $P2_1/c$, $a = 9.899$ (2), $b = 10.028$ (1), $c = 10.006$ (2) Å, $\beta = 117.20$ (1)°, $V = 883.5$ (2) Å^3, $Z = 2$, $D_x = 1.86$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 30.4$ cm^{-1}, $F(000) = 492$, $T = 299$ K, final $R = 0.034$ for 1056 reflections with $F_o \geq 3\sigma(F_o)$. The dimer