



Jahn–Teller-distorted dimeric anions in (cat)[Mn₂F₈(H₂O)₂].2H₂O (cat = pipzH₂, dabcoH₂) and (dabcoH₂)₂[Mn₂F₈(H₂PO₄)₂]

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ABSTRACT

Using biprotonated dabco (1,4-diazabicyclo[2.2.2]octane) or pipz (piperazine) as counter cations, mixed-ligand fluoromanganates(III) with dimeric anions could be prepared from hydrofluoric acid solutions. The crystal structures were determined by X-ray diffraction on single crystals: dabcoH₂[Mn₂F₈(H₂O)₂].2H₂O (**1**), space group *P2*₁, *Z* = 2, *a* = 6.944(1), *b* = 14.689(3), *c* = 7.307(1) Å, β = 93.75(3)°, *R*₁ = 0.0240; pipzH₂[Mn₂F₈(H₂O)₂].2H₂O (**2**), space group *P* $\bar{1}$, *Z* = 2, *a* = 6.977(1), *b* = 8.760(2), *c* = 12.584(3) Å, α = 83.79(3), β = 74.25(3), γ = 71.20(3)°, *R*₁ = 0.0451; (dabcoH₂)₂[Mn₂F₈(H₂PO₄)₂] (**3**), space group *P2*₁/*n*, *Z* = 4, *a* = 9.3447(4), *b* = 12.5208(4), *c* = 9.7591(6) Å, β = 94.392(8)°, *R*₁ = 0.0280. All three compounds show dimeric anions formed by [MnF₅O] octahedra (O from oxo ligands) sharing a common edge, with strongly asymmetric double fluorine bridges. In contrast to analogous dimeric anions of Al or Fe(III), the oxo ligands (H₂O (**1**, **2**) or phosphate (**3**)) are in equatorial *trans*-positions within the bridging plane. The strong pseudo-Jahn–Teller effect of octahedral Mn(III) complexes is documented in a huge elongation of an octahedral axis, namely that including the long bridging Mn–F bond and the Mn–O bond. In spite of different charge of the anion in the fluoride phosphate, the octahedral geometry is almost the same as in the aqua-fluoro compounds. The strong distortion is reflected also in the ligand field spectra.

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1. Introduction

Fluoromanganates(III) with *d*⁴-high-spin configuration are well suited to study the influence of the structural topology on extent and direction of Jahn–Teller distortions [1]. It has been shown that small distortions, in some cases even averaged by a dynamical Jahn–Teller effect, are found in compounds with isolated anions like [Co(H₂O)₆][MnF₆] [2]. The strongest distortions are encountered when the Jahn–Teller-active centers are strongly coupled, for instance in layer structures AMnF₄ (A = alkali metal, Tl), where in a square net of corner-sharing octahedra strongly asymmetrical bridges are formed (“antiferrodistortive ordering”) [3–5]. This paper deals with some rare examples where two Jahn–Teller-active Mn(III) centers are coupled in dimers of edge-sharing [MnF₅O] octahedra.

2. Results and discussion

2.1. Syntheses

dabcoH₂[Mn₂F₈(H₂O)₂].2H₂O (**1**) and pipzH₂[Mn₂F₈(H₂O)₂].2H₂O (**2**) crystallized from hydrofluoric acid solutions of manganese(III) acetate after adding an aqueous dabco or piperazine solution, respectively. (dabcoH₂)₂[Mn₂F₈(H₂PO₄)₂] (**3**) formed from a hydrofluoric acid solution of MnF₃·3H₂O after adding a solution of dabco in phosphoric acid. For details see Section 3.

2.2. Crystal structures

For all three compounds, the crystal structures could be determined by X-ray structure analyses on single crystals, the crystal data and experimental details of which are given in Section 3.

2.2.1. Compounds cat[Mn₂F₈(H₂O)₂].2H₂O (cat = dabcoH₂ (**1**), and pipzH₂ (**2**))

The structures are built from dabcoH₂²⁺ or pipzH₂²⁺ cations and [Mn₂F₈(H₂O)₂]²⁻ anions that have not been reported before (Figs. 1a and 2). In similar systems, structures comprising isolated

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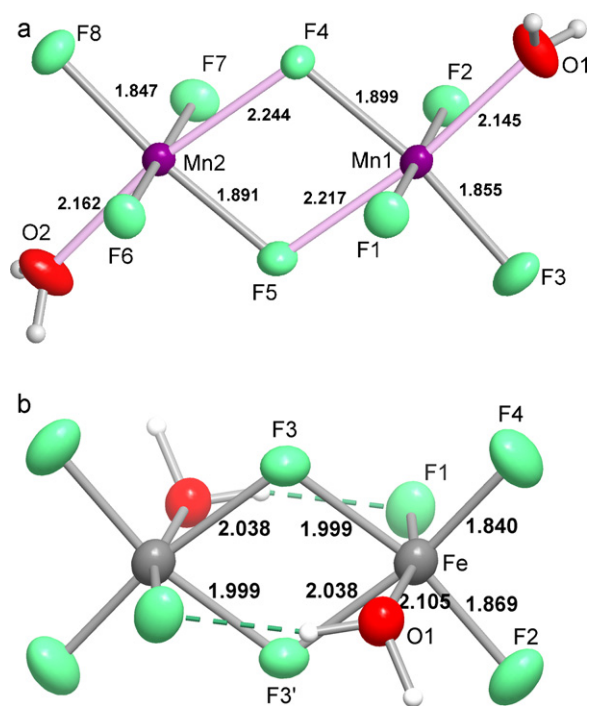


Fig. 1. (a) $[\text{Mn}_2\text{F}_8(\text{H}_2\text{O})_2]^{2-}$ anion in (1) with selected bond lengths in Å (e.s.d.s 0.0017–0.0026). (b) $[\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2]^{2-}$ anion in $[(\text{CH}_3)_4\text{N}][\text{Fe}_2\text{F}_8(\text{H}_2\text{O})_2]$ [9] with selected bond lengths in Å (e.s.d.s 0.004–0.005). Displacement ellipsoids at the 50% probability level, H atoms as spheres with arbitrary radius, intramolecular H-bonds dashed.

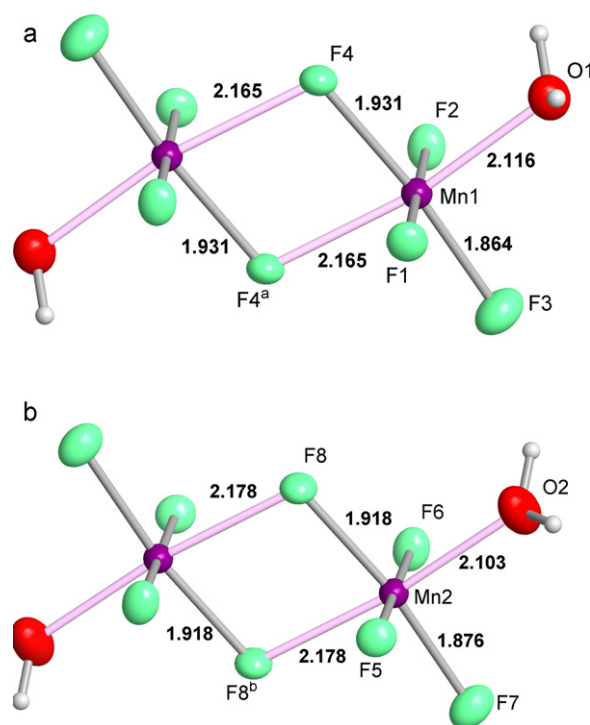


Fig. 2. (a and b) The two independent centrosymmetric anions in (2) with selected bond lengths in Å (e.s.d.s 0.0015–0.0020). Displacement ellipsoids at the 50% probability level, H atom as spheres with arbitrary radius.

anions such as $[\text{MnF}_5(\text{H}_2\text{O})_2]^{2-}$ or $[\text{MnF}_5(\text{H}_2\text{O})_2]^-$, or linear chains are observed (overview see [1]). In the dabco compound (1), the $[\text{Mn}_2\text{F}_8(\text{H}_2\text{O})_2]^{2-}$ anion has no crystallographic symmetry but approaches point symmetry $2/m$ (C_{2h}). In the pipz compound (2), there are two independent centrosymmetrical anions, both with pseudosymmetry $2/m$, too (Fig. 2). The anions can be described as dimers built from edge-sharing $[\text{MnF}_5(\text{H}_2\text{O})]$ octahedra. The occurrence of double fluorine bridges is rare in the structural chemistry of fluorides [6–8] which is dominated by the connection

of the octahedra via sharing of common vertices. Examples of dimeric anions of analogous composition were found in compounds $[(\text{CH}_3)_4\text{N}][\text{M}_2\text{F}_8(\text{H}_2\text{O})_2]$ ($\text{M} = \text{Fe}, \text{Al}$) [9]. The respective Fe(III) compound is a very good reference structure for revealing the influence of the Jahn–Teller effect of Mn(III) because the ionic radius of Fe^{3+} is the same as that of Mn^{3+} (0.645 Å) [10] but the electronic configuration is highly symmetric d^5 . In the iron compound, the position of the aqua ligands is *trans*-axial (Fig. 1b) while in both Mn(III) compounds it is *trans*-equatorial

Table 1

Bond lengths (Å) and selected angles ($^\circ$) in the anions of $\text{dabcoH}_2[\text{Mn}_2\text{F}_8(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (1), $\text{pipzH}_2[\text{Mn}_2\text{F}_8(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (2), and $(\text{dabcoH}_2)_2[\text{Mn}_2\text{F}_8(\text{H}_2\text{PO}_4)_2]$ (3).

(1)		(2)		(3)	
Mn1–F1	1.824(2)	Mn1–F1	1.817(2)	Mn–F1	1.819(1)
Mn1–F2	1.812(2)	Mn1–F2	1.824(2)	Mn–F2	1.815(1)
Mn1–F3	1.855(2)	Mn1–F3	1.864(2)	Mn–F3	1.855(1)
Mn1–F4	1.899(2)	Mn1–F4	1.931(2)	Mn–F4	1.915(1)
Mn1–F5	2.217(2)	Mn1–F4 ^a	2.165(2)	Mn–F4 ^c	2.250(1)
Mn1–O1	2.145(3)	Mn1–O1	2.116(2)	Mn–O2	2.126(1)
Mn2–F6	1.835(2)	Mn2–F5	1.810(2)	P–O1	1.497(1)
Mn2–F7	1.805(2)	Mn2–F6	1.823(2)	P–O2	1.508(1)
Mn2–F8	1.847(2)	Mn2–F7	1.876(2)	P–O3	1.563(1)
Mn2–F5	1.891(2)	Mn2–F8	1.918(2)	P–O4	1.580(1)
Mn2–F4	2.244(2)	Mn2–F8 ^b	2.178(2)		
Mn2–O2	2.162(3)	Mn2–O2	2.103(2)		
F1–Mn1–F2	178.5(1)	F1–Mn1–F2	179.2(1)	F1–Mn–F2	177.49(5)
F3–Mn1–F4	170.8(1)	F3–Mn1–F4	173.9(1)	F3–Mn–F4	169.89(4)
F5–Mn1–O1	172.4(1)	F4 ^a –Mn1–O1	170.3(1)	F4 ^c –Mn–O2	164.14(4)
F6–Mn2–F7	178.5(1)	F5–Mn2–F6	179.7(1)		
F5–Mn2–F8	173.3(1)	F7–Mn2–F8	172.0(1)		
F4–Mn2–O2	170.3(1)	F8 ^b –Mn2–O2	173.4(1)		
F3–Mn1–O1	94.5(1)	F3–Mn1–O1	93.8(1)	F3–Mn–O2	102.25(5)
F4–Mn1–F5	77.7(1)	F4–Mn1–F4 ^a	78.0(1)	F4–Mn–F4 ^c	77.94(4)
F8–Mn2–O2	93.3(1)	F7–Mn2–O2	93.0(1)		
F4–Mn2–F5	77.2(1)	F8–Mn2–F8 ^b	78.5(1)		
Mn1–F4–Mn2	101.9(1)	Mn1–F4–Mn1 ^a	102.0(1)	Mn–F4–Mn ^c	102.06(4)
Mn1–F5–Mn2	103.2(1)	Mn2–F8–Mn2 ^b	101.5(1)		

Symmetry-transformations: ^a1 – x, 1 – y, 1 – z; ^b–x, 2 – y, –z; ^c–x, 1 – y, –z.

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