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Structure of Trisodium Hexafluoromanganate(III)

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Abstract. Na_3MnF_6, $M_r = 237.90$, monoclinic, $P2_1/n$, $a = 5.4709$ (9), $b = 5.6830$ (6), $c = 8.0734$ (12) Å, $\beta = 88.964$ (7)°, $V = 250.97$ (6) Å^3, $Z = 2$, $D_x = 3.15$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 27.6$ cm^{-1}, $F(000) = 224$, $T = 293$ K, $R = 0.0152$, $wR = 0.0144$ for 550 unique reflections [$F_o > 3\sigma(F_o)$]. The structure is isostructural with that of the cryolite Na_3AlF_6 and shows the weakest static Jahn–Teller distortion known to date for $[MnF_6]^{3-}$ octahedra [d(Mn—F) axial 2.0176 (8), mean equatorial 1.880 (1) Å]. The ordering of the elongated octahedra is ferrodistortive. Of the Na ions, one third have octahedral and the remainder have bicapped trigonal prismatic eight coordination.

Introduction. Single-crystal studies on sodiumhexafluorometallates(III) $Na_3M^{III}F_6$ (M^{III} = Cr, Fe) revealed cryolite structures closely related to that of Na_3AlF_6 (Naray-Szabo & Sasvari, 1938; Hawthorne & Ferguson, 1975), space group $P2_1/n$. The Cr compound crystallizes in the same space group (Brunton, 1969), while for the structure of the iron compound $P2_1$ is assumed (Matvienko, Yakubovich, Simonov, Ivashchenko, Melnikov & Belov, 1981). For several other compounds Na_3MF_6 (M = Ga, Sc, Ti, V, Mn, Co, Ni, Cu) cryolite-type unit cells were deduced from powder diffraction data (*cf.* review of Babel & Tressaud, 1985). In the course of studies on the dependence of Jahn–Teller distortion on the structure type, we were interested in the crystal structure of the Mn^{III} compound. Na_3MnF_6 was mentioned for the first time by Siebert & Hoppe (1971). Lattice parameters have been proposed by Bucovec & Siftar (1975) ($a = 5.56$, $b = 5.84$, $c = 8.10$ Å, $\beta = 90.7°$) which were confirmed roughly by our single-crystal investigation reported here.

Experimental. The title compound was prepared by heating a stoichiometric mixture of NaF and MnF_3 in a sealed Pt tube ($T = 1123$ K for 2 d, cooling to 893 K at 19 K h^{-1}, sinter for a further 2 d, then cooling to room temperature at 48 K h^{-1}). A purple crystal with approximate dimensions 0.07 × 0.11 × 0.10 mm was used for film exposures (Buerger technique, Mo $K\alpha$ radiation) yielding a cryolite-sized cell and the space group $P2_1/n$ and for the data collection on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (Enraf–Nonius/Delft). The unit-cell parameters (conventional monoclinic setting with $\beta = 91.04°$) were refined on the basis of the diffraction angles of 25 reflections with θ between 15 and 23°, each determined from measurements in the positive and negative θ range. The intensities of 1329 reflections were measured (θ = 2–28°, h: -7 to 7, k: 0 to 7, l: -10 to 10), using ω scans over $(1.2 + 0.35\tan\theta)°$ and an additional 25% before and after each reflection for background measurements. The variable measuring time was a maximum 36 s per reflection. 550 observed reflections [with $F_o > 3\sigma(F_o)$] obtained after merging (605 unique reflections, R_{int} 0.016) were used for calculations. An empirical absorption correction (μ = 27.6 cm^{-1}) was applied based on ψ scans with nine strong reflections well distributed in reciprocal space (minimum/maximum transmission factors 0.84/0.99). Starting in the conventional set up of the unit cell with $\beta = 91.04°$ it was not possible to refine a cryolite model with parameters taken from Na_3AlF_6 (Hawthorne & Ferguson, 1975). Thus, the structure was solved from a Patterson map and refined by the full-matrix least-squares method minimizing $\sum w(\Delta F)^2$ with weights $w = 1/\sigma^2$ (*SHELXTL-Plus*; Sheldrick, 1989). However, the resulting structure did prove to be a cryolite, but the equivalent parameter set – comparable directly with that of Na_3AlF_6 and Na_3CrF_6 – refers to the transformed cell [transformation matrix ($\bar{1}00$, $0\bar{1}0$, 001)] with $\beta = 88.96°$. The non-conventional setting of a monoclinic cell was chosen for this reason. For all atoms anisotropic temperature factors could be applied. Using scat-

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Table 1. *Atomic coordinates and anisotropic temperature factors* (Å^2) *for* Na_3MnF_6

$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$.

	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	2(*a*)	0.0	0.0	0.0	0.0102 (1)	0.0092 (1)	0.0101 (1)	0.0000 (1)	0.0008 (1)	0.0003 (1)
Na1	2(*b*)	0.0	0.0	0.5	0.0164 (3)	0.0148 (3)	0.0134 (3)	0.0022 (3)	−0.0006 (3)	−0.0017 (3)
Na2	4(*e*)	0.50923 (10)	−0.05464 (10)	0.24988 (7)	0.0227 (3)	0.0202 (3)	0.0292 (3)	0.0013 (2)	0.0006 (2)	−0.0036 (2)
F1	4(*e*)	0.1148 (2)	0.0578 (1)	0.2326 (1)	0.0241 (4)	0.0219 (5)	0.0155 (3)	0.0005 (3)	−0.0003 (3)	0.0025 (3)
F2	4(*e*)	−0.2807 (1)	0.1713 (1)	0.0533 (1)	0.0205 (4)	0.0218 (4)	0.0250 (4)	0.0036 (3)	0.0050 (3)	0.0079 (4)
F3	4(*e*)	0.1632 (2)	0.2795 (1)	−0.0674 (1)	0.0228 (4)	0.0195 (4)	0.0262 (4)	0.0053 (3)	−0.0035 (3)	−0.0045 (4)

Table 2. *Interatomic distances* (Å) *and selected angles* (°) *for* Na_3MnF_6

Mn—F1, F1^{i}	2.0176 (8)	Na2—F1	2.257 (1)
Mn—F2, F2^{i}	1.8621 (8)	Na2—F1^{vi}	2.309 (1)
Mn—F3, F3^{i}	1.8969 (9)	Na2—F2^{vi}	2.691 (1)
Na1—F1, F1^{ii}	2.262 (1)	Na2—F2^{vii}	2.329 (1)
Na1—F2^{iii}, F2^{iv}	2.266 (1)	Na2—F2^{i}	2.847 (1)
Na1—F3^{v}, F3^{vi}	2.302 (1)	Na2—F3^{iii}	2.319 (1)
Mean Mn—F	1.925	Na2—F3^{viii}	2.631 (1)
Mean Na1—F	2.277	Na2—F3^{vi}	2.874 (1)
		Mean Na2—F	2.532
F1—Mn—F2	88.24 (3)	F1—Na1—F2^{iv}	94.43 (3)
F1—Mn—F2^{i}	91.76 (3)	F1—Na1—F2^{iii}	85.57 (3)
F1—Mn—F3	88.73 (3)	F1—Na1—F3^{vi}	95.45 (3)
F1—Mn—F3^{i}	91.27 (3)	F1—Na1—F3^{v}	84.55 (3)
F2—Mn—F3	90.60 (4)	F2^{iv}—Na1—F3^{vi}	91.43 (3)
F2—Mn—F3^{i}	89.40 (4)	F2^{iv}—Na1—F3^{v}	88.57 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $1+x, y\ z$; (viii) $1-x, -y, -z$.

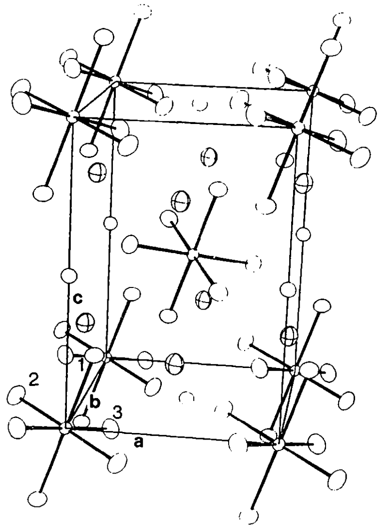

Fig. 1. The unit cell of Na_3MnF_6 (*ORTEP*; Johnson, 1965). Na1 open circles, Na2 ellipsoids, only the Mn—F bonds are depicted.

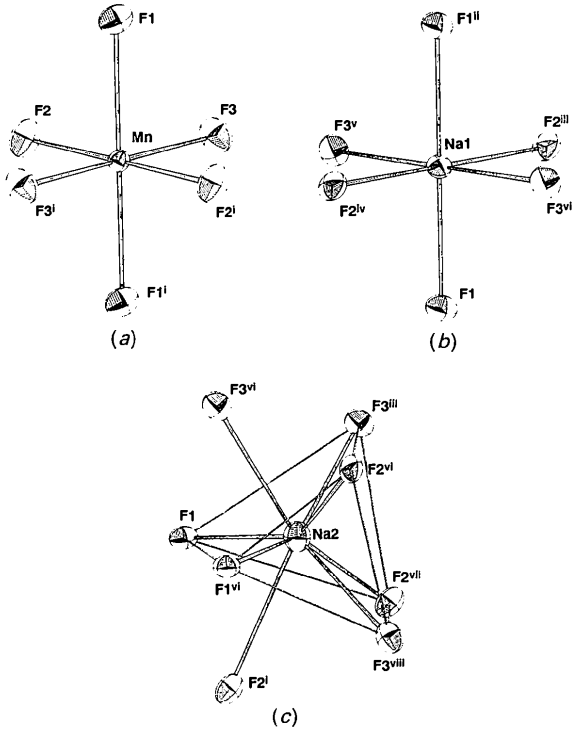

Fig. 2. The coordination polyhedra of (*a*) Mn^{3+}, (*b*) Na1 and (*c*) Na2 (*ORTEP*). Thermal ellipsoids at the 50% probability level. The indices refer to the symmetry codes of Table 2.

tering factors for neutral atoms including anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (Cromer & Mann, 1974) the refinement (49 parameters) converged to $R = 0.0168$, $wR = 0.0179$. With the scattering factors for ions, the residuals dropped to $R = 0.0152$ and $wR = 0.0144$. The parameter shifts in the last cycle were all less than 0.004 × e.s.d., the maximum and minimum heights in a final $\Delta\rho$ synthesis were 0.24 and -0.21 e Å^{-3}. Final atomic coordinates and anisotropic thermal parameters based on the ionic model are given in Table 1 and selected interatomic distances and angles in Table 2.*

Discussion. The crystal structure of Na_3MnF_6 shows the typical cryolite arrangement of quasi-isolated MnF_6 octahedra (Fig. 1) separated by two crystallographically different kinds of Na cations. The influence of the Jahn–Teller effect on the Mn^{3+} ion (d^4 high spin) may be best extracted by comparing the

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54475 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0476]

structural geometry with that of the isostructural Cr^{3+} (d^3) cryolite. While in the latter compound, as in the Al and Fe cryolites, the MF_6 octahedra are nearly regular (Cr—F 1.900–1.907 Å), the MnF_6 group is elongated with $Mn—F_{ax} = 2.018$ and a mean $Mn—F_{eq} = 1.880$ Å (Table 2, Fig. 2*a*). In terms of relative bond strengths (Massa & Babel, 1988) the axial bonds are weakened by 23%. Nevertheless, this remarkable effect is the smallest among all known structures with ordered statically distorted MnF_6 groups. The reason must be the weak coupling of the quasi-isolated (MnF_6) groups in the lattice. One-, two-, three-dimensional connection leads to a stronger cooperative Jahn–Teller effect. Comparing the geometry of the (MnF_6) units to that in other sodium fluoromanganates, for instance, we find in the chain compound Na_2MnF_5 axial/mean equatorial Mn—F bond lengths of 2.109/1.849 Å (Massa, 1986) and in the layer structure of $NaMnF_4$ 2.167/1.839 Å (Molinier, Massa, Khairoun, Tressaud & Soubeyroux, 1991). The ordering of the elongated octahedra is ferrodistortive. The long axes point roughly towards the *c* axis but are inclined at about 20°, similar to the Cr compound (Fig. 1). Owing to the *n*-glide operation, the octahedra on the corners of the unit cell and at the centre are inclined to each other by 18.7° (Cr 18.5°). Na1 has a weakly distorted octahedral coordination, while the Na2 cation has an eight-coordinated surrounding of F^- ions best described as a distorted bicapped trigonal prism (Table 2, Fig. 2*c*).

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Structure of the Cyclic Barium Copper Silicate $Ba_2Cu_2[Si_4O_{12}]$ at 300 K

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Abstract. Dibarium dicopper tetrasilicate, $Ba_2Cu_2Si_4O_{12}$, $M_r = 706{\cdot}1$, tetragonal, *I*4/*mmm*, $a = 7{\cdot}0515$ (20), $c = 11{\cdot}1503$ (30) Å, $V = 554{\cdot}4$ (4) Å^3, $Z = 2$, $D_x = 4{\cdot}228$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 113{\cdot}0$ cm^{-1}, $F(000) = 644$, $T = 300$ K, final $R = 0{\cdot}0300$ for 97 unique reflections [313 observed with $|F_o| > 3\sigma(|F_o|)$]. The structure contains isolated cyclic $[Si_4O_{12}]^{8-}$ groups, Si—O(1) = 1·570 (10), Si—O(2) = 1·602 (4) Å in the ring system. The copper cation is square coordinated by four O(1) atoms, Cu—O(1) = 1·925 (11) Å. The barium cation is surrouned by a square antiprism formed by eight O(1) atoms, Ba—O(1) = 2·930 (5) Å, and four O(2) atoms at 3·263 (8) Å.

Introduction. The title compound is the second barium copper silicate obtained during our studies of the chemcial reactivity of the '1-2-3' type superconductors. Results on the synthesis and crystal structure of $BaCu_2Si_2O_7$ which was obtained in the reaction of $YBa_2Cu_3O_{7-x}$ with SiO_2 in the presence of Bi_2O_3 have been published previously (Janczak,

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