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The Mixed Anionic Framework in the Structure of $Na_2\{MnF[PO_4]\}$

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Abstract

In the crystal structure of hydrothermally synthesized disodium manganese fluoride orthophosphate, $Na_2\{MnF[PO_4]\}$, two kinds of *cis*-MnO_4F_2 octahedra share common vertices to form $(Mn_2F_2O_8)$ chains parallel to the *b* axis of the monoclinic unit cell. In the *a* and *c* directions these chains are linked by PO_4 tetrahedra to form a three-dimensional framework of octahedra and tetrahedra. Na^+ cations are located in the channels of this framework structure. The problem of $\{OTX_5\}$ mixed anionic radical polymorphism is discussed.

Comment

This work is part of our efforts to synthesize and investigate pegmatite-related phosphates. We are interested in the relationship between the structures of transition metal phosphates and the conditions of their formation (Yakubovich & Urusov, 1996). In addition to this, first row transition metal phosphates have become a focus for interest in recent years because of their possible use as new non-linear optical materials such as $KTiOPO_4$ (KTP). The crystals of the new compound, $Na_2\{MnF[PO_4]\}$, were obtained as the product of hydrothermal growth experiments in the system NaF–MnO–$(NH_4)_2HPO_4$–H_2O.

The manganese octahedra in $Na_2\{MnF[PO_4]\}$ share common F vertices to form $(Mn_2F_2O_8)$ chains parallel to the *b* axis of the unit cell (Fig. 1). Four vertices of each manganese octahedron are occupied by O atoms, and two by F atoms in *cis* positions. The Mn1—O and Mn2—O distances do not differ significantly and lie in the range 2.132 (3)–2.171 (3) Å (Table 1). The variation of the Mn—F distances is substantially greater, 2.154 (2)–2.305 (2) Å. One of the four P—O distances in each of the two independent phosphate tetrahedra is larger [1.555 (3) and 1.552 (3) Å] than the other three distances, which lie in the range 1.531 (3)–1.535 (3) Å (the P1 tetrahedron) or are 1.537 (3) Å (the P2 tetrahedron).

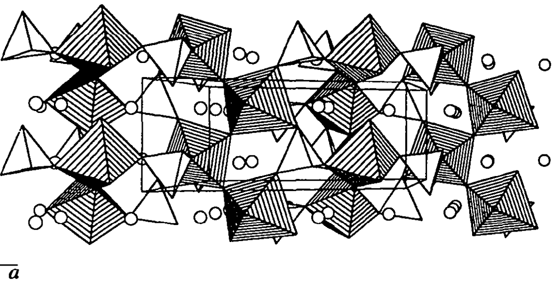

Fig. 1. A perspective view along the *c* axis. Na^+ cations are represented as spheres.

There are four $(Mn_2F_2O_8)$ chains in the unit cell (Fig. 2). The two kinds of these chains, which are parallel to the *b* axis, comprise Mn1 (the first type) or Mn2 (the second type) polyhedra. In the *a* and *c* directions, these octahedral chains are linked by PO_4 tetrahedra to give a three-dimensional framework. Each of the Mn1 and Mn2 polyhedra shares two F vertices with two neighbouring octahedra and four O vertices with different PO_4 tetrahedra.

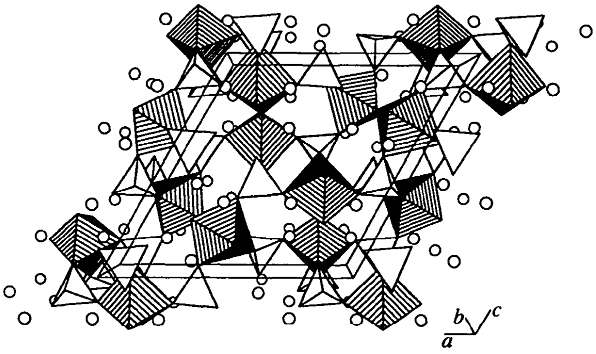

Fig. 2. A perspective view of the mixed anionic framework along the octahedral chain direction.

Four types of independent Na^+ ions in general positions occupy the interstices of this framework. They form quite regular (NaF_2O_4) octahedra with Na—F distances in the range 2.262 (3)–2.457 (3) Å and Na—O distances between 2.328 (3) and 2.525 (4) Å. The open structure of the anionic framework exhibits several crossed channels (Fig. 2) suggesting possible cationic (Na^+) transport properties.

The structure type determined for $Na_2\{MnF[PO_4]\}$ has been found earlier for two zirconium compounds: $Na_2\{ZrO[SiO_4]\}$ (Treushnikov, Iluhin & Belov, 1970) and $Na_2\{ZrO[GeO_4]\}$ (Nocirev, Treushnikov, Iluhin & Belov, 1974). In these structures, zirconium plays the part of manganese, silicon or germanium replace phosphorus, and the function of the F atoms is adopted by the additional O atom. The Zr atoms in both structures occupy quite regular octahedra with Zr—O distances in the ranges 1.99–2.17 Å (for the silicate) and 1.98–2.20 Å (for the germanate). The mixed anionic framework is formed from chains of Zr octahedra and SiO_4 or GeO_4 tetrahedra. These chains are parallel to the *b* axis. The formula of the anionic radicals in these three phases can be written (after Sandomirskji & Belov, 1984) as $\{OTX_5\}$, where *O* and *T* are octahedrally and tetrahedrally coordinated cations, respectively, and *X* is an anion.

Four topologically different structure types with the anionic construction $\{OTX_5\}$ are now known. Among them there are three which have three-dimensional frameworks of octahedra and tetrahedra. Typical structures are: titanite ($Ca\{TiO[SiO_4]\}$) and isostructural phosphates and arsenates (type 2; Lahti & Pajunen, 1985), namely lacroixite ($NaAlFPO_4$), durangite ($NaAlFAsO_4$), amblygonite [$LiAl(F,OH)PO_4$], synthetic phases $NaTiOPO_4$ and $NaVOPO_4$; $K\{TiO[PO_4]\}$ (KTP; Tordjman, Masse & Guitel, 1974), its structural analogues $KGeOPO_4$, $KVOPO_4$, $KSnOPO_4$, $KTiOAsO_4$, $KFeFPO_4$ and many others (type 3); $Na_2\{MnF[PO_4]\}$ and the isostructural compounds $Na_2ZrOSiO_4$ and $Na_2ZrOGeO_4$ (type 4). The topological difference between these frameworks is based on the connection of the octahedra within the chains. In the titanite structure type, the octahedra are linked *via trans* vertices to form linear chains. Na_2MnFPO_4 contains *cis* connected octahedra and the chains in KTP are formed by octahedra linked alternately *via trans* and *cis* vertices.

The mixed anionic layers in the natisite ($Na_2\{TiO[SiO_4]\}$) structure type are formed from five-vertex titanium polyhedra and silicate tetrahedra. The change from Ti^{4+} to Fe^{3+} in the cationic matrix of the mixed anionic radical results (as shown earlier; Yakubovich, Mel'nikov & Urusov, 1995) in an increase in the degree of polymerization of this radical from layers in natisite to a *para*-framework in $Na_{1.5}\{FeF_{1.5}[PO_4]\}$. The small change in the formula of the radical from $\{OTX_5\}$ to $\{OTX_{5.5}\}$ (as the Fe octahedra have one more vertex than the Ti pyramids) keeps the topology of the radical the same in the layer projection and allows these constructions to be united in one structure type.

These polymorphic and quasi-polymorphic transformations of the mixed anionic radicals $\{OTX_5\}$ have allowed us to distinguish four morphotropic series of compounds differing in the topology of their anionic construction. The *OT* anionic radical polymorphism is described by morphotropic or homologous kinds of transitions. This polymorphism is caused by the change of the number or size of atoms forming the cationic subcell of the structures. The change of the degree of polymerization of the anionic complex within the same morphotropic series is due to the chemical transformation of anionic *OT* radicals.

Experimental

Single crystals were obtained by hydrothermal synthesis in the system $NaF–MnO–(NH_4)_2HPO_4–H_2O$ [T = 623 K, P = 1000 atm (1 atm = 101325 Pa), 50% aqueous solution of NaF, $MnO:(NH_4)_2HPO_4$ = 1:1]. X-ray spectral analysis (CAMSCAN 4DV) revealed the presence of sodium, manganese and phosphorus in the ratio 2:1:1 in the grown material.

Crystal data

$Na_2\{MnF[PO_4]\}$
$M_r = 214.89$
Monoclinic
$P2_1/n$
$a = 13.683\ (3)$ Å
$b = 5.3170\ (10)$ Å
$c = 13.717\ (3)$ Å
$\beta = 119.67\ (3)°$
$V = 867.1\ (3)$ Å^3
$Z = 8$
$D_x = 3.292$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 10–25°$
$\mu = 3.546$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.4 × 0.2 × 0.08 mm
Colourless

Data collection

Syntex $P\bar{1}$ diffractometer
$2\theta–\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.691$, $T_{max} = 0.753$
4888 measured reflections
2862 independent reflections

2849 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0301$
$\theta_{max} = 48.78°$
$h = -27 \rightarrow 23$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 26$
1 standard reflection every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.097$
$S = 1.292$
2862 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 1.8351P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.905$ e Å^{-3}
$\Delta\rho_{min} = -1.102$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0138 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Mn1—O7^{i}	2.132 (3)	Na2—F2^{x}	2.291 (3)
Mn1—O3^{ii}	2.139 (3)	Na2—O6	2.387 (3)
Mn1—F2	2.154 (2)	Na2—O7^{x}	2.404 (3)
Mn1—O6^{iii}	2.154 (3)	Na2—O3^{ii}	2.405 (3)
Mn1—O2	2.169 (3)	Na2—F2^{iv}	2.435 (3)
Mn1—F2^{iv}	2.305 (2)	Na2—O2	2.502 (4)
Mn2—O1^{v}	2.141 (3)	Na3—O2	2.328 (3)
Mn2—O4	2.144 (3)	Na3—F2^{iv}	2.335 (3)
Mn2—O8	2.159 (3)	Na3—O3^{viii}	2.367 (3)
Mn2—O5^{vi}	2.171 (3)	Na3—O4	2.416 (3)
Mn2—F1^{vii}	2.173 (2)	Na3—F2	2.429 (3)

Mn2—F1	2.294 (2)	Na3—$O6^{v}$	2.525 (4)
Na1—$F1^{viii}$	2.262 (3)	Na4—$O5^{xi}$	2.343 (3)
Na1—O4	2.383 (3)	Na4—$F1^{vii}$	2.346 (3)
Na1—$O8^{viii}$	2.407 (3)	Na4—O1	2.360 (3)
Na1—$O5^{v}$	2.412 (3)	Na4—$O7^{x}$	2.400 (3)
Na1—$O1^{vi}$	2.420 (3)	Na4—$F1^{x}$	2.407 (3)
Na1—$F1^{ix}$	2.457 (3)	Na4—O8	2.500 (4)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $x, y-1, z$; (vi) $1-x, 1-y, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $1-x, -y, 1-z$; (x) $x, 1+y, z$; (xi) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$.

The formula of the new compound was established by the structural investigation. The absence of OH groups was confirmed by IR spectral analysis. The minimum residual electron density peak of -1.102 e Å^{-3} is located 0.79 Å from P1.

Data collection: Syntex $P\bar{1}$ software. Cell refinement: Syntex $P\bar{1}$ software. Data reduction: Syntex $P\bar{1}$ software. Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *STRUPLO*84 (Fischer, 1985), *TROMPLEU* (Le Lirzin, Gravereau & Larroche, 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry, and a displacement ellipsoid drawing plotted at the 60% probability level have been deposited with the IUCr (Reference: AB1400). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Na_4Ce(As_2O_7)_2$

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Abstract

Tetrasodium cerium(IV) bis[diarsenate(4−)] is built from CeO_8 antiprisms and As_2O_7 diarsenate groups connected by Ce—O—As mixed bridges to form a three-dimensional framework. The As_2O_7 diarsenate groups have a nearly eclipsed conformation. The framework delimits interconnecting tunnels running along the [001] and [110] directions where the Na^+ cations are located.

Commentaire

Les composés de formulation $A^{I}M^{III}X_2O_7$ (X = As, P) (Boughzala, Driss & Jouini, 1993), ont fait l'objet de nombreux travaux en raison de leurs proprietés potentielles (conduction ionique ou protonique, échange d'ions, catalytique). En revanche nous n'avons relevé dans la bibliographie aucun composé faisant intervenir le degré d'oxydation IV, qui aurait pour formulation $A^{I}_4M^{IV}(X_2O_7)_2$. C'est pour cette raison que nous avons entrepris l'investigation du système Na_2O–CeO_2–X_2O_5, (X = As, P) dans lequel nous venons de mettre en évidence le composé $Na_4Ce(As_2O_7)_2$.

Les ellipsoïdes d'agitation thermique et la désignation des atomes sont représentées à la Fig. 1.

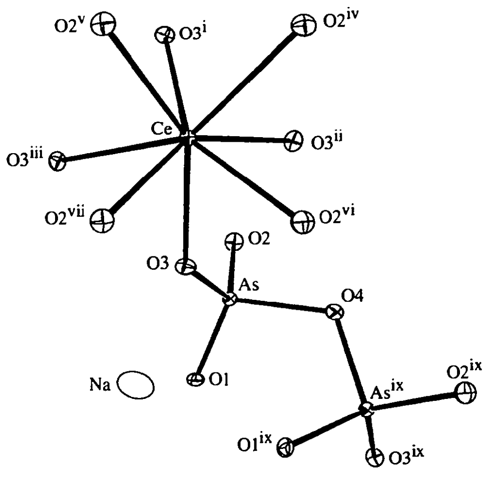

Fig. 1. Représentation *ORTEP*II (Johnson, 1976) de la connexion d'un antiprisme CeO_8 et d'un groupement diarséniate. Les ellipsoïdes d'agitation thermique correspondent à 50% de probabilité, les codes de symétrie sont définis au Tableau 2.