larger than the monatomic cations, there are also short intermolecular contacts for the nitrosyl and carbonyl groups, the shortest O···O distance being 3.075 (10) Å. These simply represent close packing of the ions, rather than any significant specific interactions. Iron atoms are all at least 5.677 (2) Å apart. In summary, the structure of (2) [as well as that of (1)] is ionic, with no Tl—Fe or Tl—Tl covalent bonding.

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Structure of Pb₂MnFe₂F₁₂.3H₂O

BY A. LE BAIL AND A. M. MERCIER

Laboratoire des Fluorures, URA 449, Université du Maine, 72017 Le Mans CEDEX, France

Abstract. Diiron dilead manganese dodecafluoride trihydrate, $M_r = 863.06$, hexagonal, $P\bar{6}2m$, $a = 9.320$ (1), $c = 3.9618$ (5) Å, $V = 298.0$ (1) Å^3, $Z = 1$, $D_x = 4.81$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 31.95$ mm^{-1}, $F(000) = 337$, room temperature, $R = 0.032$ for 845 unique reflections, crystal growth by hydrothermal synthesis in HF solution. The structure presents three chains of MF_6 octahedra ($M = Fe^{3+}$, Mn^{2+} statistically distributed on the same site) sharing *trans* corners along [001] and connected by *cis* corners to form a triple infinite isolated chain of formula $[M_3F_{12}]_n^{4n-}$. The structure is related to the CsCrF₄ type; however, the Cs-atom site is occupied by the water molecule and the Pb atom occupies a trigonal prism of F atoms tricapped by the water molecules.

Introduction. Investigations of PbF₂–FeF₃–MF_2–HF$_{aq}$ systems ($M = $ Mn, Zn, Cu) by hydrothermal synthesis reveal to date two new low-dimensional structure types. One of them, having the Pb₈MFe₂F₂₄ formulation, is characterized by a structure containing infinite isolated $[MFe_2F_{14}]_n^{6n-}$ chains of corner-sharing octahedra inserted into a fluorite-like matrix (Le Bail & Mercier, 1991). The second structure type is that of Pb₂MnFe₂F₁₂.3H₂O, whose determination is presented here; it is built up from completely different condensed chains.

Experimental. A few hexagonal prismatic light brown single crystals of Pb₂MnFe₂F₁₂.3H₂O were grown by hydrothermal synthesis in 1 M HF solution following a procedure described by Plet, Fourquet, Courbion, Leblanc & De Pape (1979). Platinum tube, volume 4.41 cm^3, filling rate 60%, 1.25 × 10^{-3} mol of nominal composition Pb₂MnFe₂F₁₂ in 2.5 cm^3 1 M HF, heating rate 300 K h^{-1}, final temperature $T_f = 573$ K, stage to reach T_f 3 d, cooling rate 30 K h^{-1}, initial pressure 100 MPa, P at T_f = 160 MPa. Phases also present: Pb₈MnFe₂F₂₄ and at least one other, currently being investigated.

Data collected on a Siemens AED-2 four-circle diffractometer. Prismatic crystal 0.13 × 0.10 × 0.12 mm. ω–2θ step-scan mode in 36 steps of $\Delta\omega = 0.035°$. Time per step $t_{min} = 1$ s, $t_{max} = 4$ s. Lattice constants based on 30 reflections at $2\theta \simeq 30°$. Absorption correction by the Gauss method $A_{max} = 0.17$, $A_{min} = 0.06$. Intensity measurement of two independent sets to $2\theta_{max} = 90°$ within the range $-18 \le h \le 18$, $-18 \le k \le 18$, $0 \le l \le 8$. Standard reflections $\bar{4}21$, $\bar{2}1\bar{2}$, $\bar{2}4\bar{1}$, intensity variation 1.0%. 2557 reflections measured, 845 independent reflections used for refinements [$|F| > 6\sigma(|F|)$], $R_{av} = 0.040$. Structure solved by Patterson method. F magnitudes used in least-squares refinements, 26 parameters refined, $\Delta/\sigma_{max} = 0.001$, secondary extinction $x = 0.0059$ (5), scattering factors for Pb^{2+}, Mn^{2+},

Table 1. *Coordinates, equivalent isotropic temperature factors* ($Å^2$) *and anisotropic temperature factors* ($U_{ij} \times 10^4$) *for* $Pb_2MnFe_2F_{12}.3H_2O$ (M = Mn, Fe) *with e.s.d.'s in parentheses*

$$U_{13} = U_{23} = 0.$$

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j.$$

	Site	x	y	z	B_{eq}
Pb	2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1.46 (1)
M	3(f)	0.7599 (1)	0	0	0.51 (3)
F(1)	6(j)	0.5293 (5)	0.8203 (6)	0	1.60 (18)
F(2)	3(g)	0.7609 (8)	0	$\frac{1}{2}$	1.95 (29)
F(3)	3(f)	0.1770 (8)	0	0	1.87 (25)
O(w)	3(g)	0.4081 (9)	0	$\frac{1}{2}$	1.99 (31)

	U_{11}	U_{22}	U_{33}	U_{12}
Pb	185 (1)	185 (1)	184 (1)	92 (1)
M	65 (2)	65 (2)	65 (2)	33 (1)
F(1)	124 (13)	217 (16)	215 (16)	46 (11)
F(2)	276 (20)	347 (33)	140 (19)	174 (16)
F(3)	221 (20)	142 (19)	319 (31)	71 (10)
O(w)	244 (20)	278 (31)	245 (29)	139 (16)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* $Pb_2MnFe_2F_{12}.3H_2O$ (M = Mn, Fe) *with e.s.d.'s in parentheses*

2 × M—F(1)	1.956 (4)	6 × Pb—F(1)	2.587 (3)
2 × M—F(2)	1.981 (1)	3 × Pb—O(w)	2.824 (2)
2 × M—F(3)	2.009 (2)	$\langle d \rangle$	2.666
$\langle d \rangle$	1.982		
F(1)—F(1)	2.901 (6)	F(1)—M—F(1)	95.7 (4)
F(1)—F(2)	2.788 (4)	F(1)—M—F(2)	90.2 (2)
F(1)—F(3)	2.725 (9)	F(1)—M—F(3)	86.8 (3)
F(2)—F(3)	2.817 (4)	F(2)—M—F(3)	89.8 (3)
F(3)—F(3)	2.857 (5)	F(3)—M—F(3)	90.6 (2)
		F(2)—M—F(2)	179.5 (1)
		F(3)—M—F(1)	117.4 (3)
2 × M—M	3.876 (2)	M—F(3)—M	149.4 (1)
2 × M—M	3.962 (1)	M—F(2)—M	179.5 (1)
4 × M—Pb	4.127 (1)		
2 × O(w)—F(3)	2.926 (8)	F(3)—O(w)—F(3)	85.2 (3)
4 × O(w)—F(1)	3.146 (7)		
4 × O(w)—F(1)	3.168 (5)		

Fe^{3+}, F^- ions from *International Tables for X-ray Crystallography* (1974, Vol. IV) and for O^{2-} from Suzuki (1960). Calculations with *SHELX*76 (Sheldrick, 1976) on a MicroVAX II computer. Refinements of the scale factor and the isotropic thermal parameter of the Pb atom on the 2(d) Wyckoff position lead to $R = 0.246$. The residual decreases to $R = 0.091$ when adding two Fe and one Mn atom statistically distributed on the 3(f) site and to $R = 0.034$ with all atoms in the isotropic thermal-motion approximation. Final $R = 0.032$ ($wR = 0.033$) using anisotropic thermal parameters for all atoms. Maximum and minimum heights in final difference map 3.3 and -3.9 e $Å^{-3}$ in the vicinity of the Pb atom. $w = 2.09/[\sigma^2(|F_o|) + 0.00059F_o^2]$. Absolute-configuration choice confirmed by $R = 0.091$ using coordinates $-x, -y, -z$. H atoms not located. No superstructure detected by careful check of long-time exposures from photographic diffraction techniques.

Discussion. The final atomic coordinates and aniso-tropic temperature factors are listed in Table 1,* selected bond lengths and angles are in Table 2. The relation with the $CsCrF_4$-type structure (Babel & Knoke, 1978) also adopted by $CsAlF_4$ (Lösch & Hebeker, 1979; Fourquet, Plet, Courbion, Bulou & De Pape, 1979) is clear from Fig. 1. In both struc-tures, the condensed $(M_3F_{12})_n$ infinite isolated chains are similar. Differences are as follows: the chain charge is $3n^-$ when $M = Cr^{3+}$ or Al^{3+} and $4n^-$ when it is ($\frac{2}{3}Fe^{3+}$, $\frac{1}{3}Mn^{2+}$); the 2(d) and 3(g) posi-tions respectively empty and occupied by the Cs atom in $CsCrF_4$ are occupied by the Pb atom and the water molecule O(w) in $Pb_2MnFe_2F_{12}.3H_2O$. The Pb atom is coordinated by a trigonal prism of F atoms F(1) tricapped by the water molecules. The mean M—F distance is in agreement with the $\frac{1}{3}$, $\frac{2}{3}$ contri-butions of Mn—F (2.115 Å) and Fe—F (1.93 Å) distances of Shannon (1976), giving 1.992 Å. In such a structure, some Mn/Fe ordering in each chain cannot be excluded because it would not be disclosed by diffraction owing to the lack of correlation between neighbouring chains. Therefore, $Pb_2MnFe_2F_{12}.3H_2O$ is described here by a mean stucture; on the other hand, disorder was also sug-gested to characterize $CsCrF_4$ for which the different
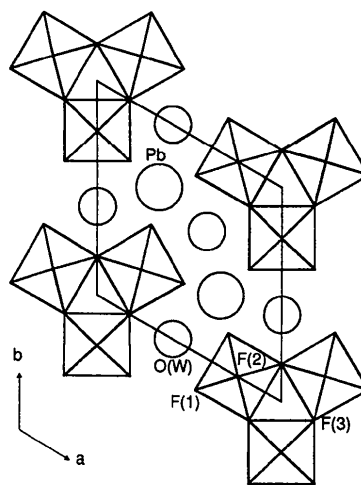
Fig. 1. (001) projection of the structure of $Pb_2MnFe_2F_{12}.3H_2O$. Large circles are Pb atoms ($z = \frac{1}{4}$), small circles are O(w) ($z = \frac{1}{4}$); M = Mn, Fe occupies octahedra ($z = 0$) formed by F(1), F(3) at $z = 0$ and F(2) ($z = \frac{1}{2}$).

anisotropic thermal-motion behaviour of the equatorial and apical F atoms was interpreted as the consequence of a probable tilting of the chains along the c axis (Babel & Knoke, 1978); such behaviour is also observed for $Pb_2MnFe_2F_{12}.3H_2O$ with the apical F(2) and equatorial F(3) strongly distributed in the ab plane and in the c direction (see U_{ij}, Table 1) respectively. Nevertheless, as usual, the terminal F atom F(1) corresponds to a shorter M—F distance than the bridging ones [F(2), F(3)]. Although H atoms have not been located, the O(w)—F(3) distance, distinctly shorter than the other O(w)—F distances (Table 2), suggests that hydrogen bonding may occur through F(3); thus the H atom could occupy an $(x0z)$ $6(i)$ position with $x \simeq 0.35$, $z \simeq 0.30$. Another related material showing triangular isolated octahedral chains is $KCrF_4$ (Dewan & Edwards, 1986; Kissel & Hoppe, 1987). Thermal behaviour and magnetic properties are now being investigated. Possible isotypic materials are being researched.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XIX. Structure of Barium *cyclo*-Hexaphosphate Octahydrate

By Mohamed Rzaigui

Ecole Normale Supérieure, 7021 Zarzouna Bizerte, Tunisia

and Marie-Thérèse Averbuch-Pouchot and André Durif

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France

Abstract. $Ba_3P_6O_{18}.8H_2O$, $M_r = 1029.966$, monoclinic, $C2/c$, $a = 20.98$ (2), $b = 7.227$ (3), $c = 17.44$ (1) Å, $\beta = 119.56$ (3)°, $V = 2300$ (5) Å^3, $Z = 4$, $D_x = 2.974$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.7017$ Å, $\mu = 5.764$ mm^{-1}, $F(000) = 1928$, $T = 294$ K, final $R = 0.041$ for 2699 reflections. The atomic arrangement can be described as being built of two layers of BaO_8 and BaO_{10} polyhedra approximately centred by planes $z = \frac{1}{4}$ and $\frac{3}{4}$ interconnected through the external oxygen atoms of the large P_6O_{18} groups. Inside a layer the Ba polyhedra assemble to form rings of eight polyhedra tiling the plane. The phosphoric ring anion has a twofold internal symmetry rarely observed in the crystal chemistry of *cyclo*-hexaphosphates. Hydrogen atoms could not be located.

Introduction. From a structural point of view very little is known about divalent cation *cyclo*-hexaphosphates. The chemical preparation and crystal structure of the cadmium salt, $Cd_3P_6O_{18}.6H_2O$, were first reported by Averbuch-Pouchot (1989*a*), later on the chemical preparation and characterization of the isotypic manganese salt were described by Averbuch-Pouchot & Durif (1989). The chemical preparation and crystal structure of the copper salt, Cu_3-$P_6O_{18}.14H_2O$, have also been reported by Averbuch-Pouchot (1989*b*). Some chemical investigations by Lazarevski, Kubasova, Chudinova & Tananaev (1980, 1982*a,b*) showing the existence of several hydrated compounds, $Cd_3P_6O_{18}.16H_2O$, $Mn_3P_6O_{18}.9H_2O$, $Co_3P_6O_{18}.14H_2O$, $Ni_3P_6O_{18}.17H_2O$ and $Cu_3P_6O_{18}.14H_2O$, should also be mentioned. The