American Mineralogist, Volume 85, pages 1534–1539, 2000

$Na_2Ca_2(P_2O_7)F_2$, the first diphosphate of the cuspidine family

A. PIOTROWSKI, V. KAHLENBERG, AND R.X. FISCHER*

Universität Bremen, Fachbereich Geowissenschaften (Kristallographie), Klagenfurter Strasse, D-28359 Bremen, Germany

ABSTRACT

The crystal structure of synthetic $Na_2Ca_2(P_2O_7)F_2$ was solved from single crystal X-ray diffraction data and refined to $R = 4.31\%$ for 1234 independent reflections [$I>2\sigma(I)$]. The compound is monoclinic with space group symmetry $P2_1/n$, $a = 10.8730(21)$ Å, $b = 10.5516(25)$ Å, $c = 7.4287(13)$ Å, and $\beta = 109.74(2)°$ and twinned by pseudo-merohedry with $m_{(100)}$ as the plane of twinning which was accounted for in the refinement calculations. The crystal belongs to the structure family of the mineral cuspidine and represents the first phosphate member of this group. The structure is characterized by ribbons of four MX_6-octahedra (M = Na,Ca; X = O,F) running parallel to **c**. Within a single ribbon the octahedra are linked by edge-sharing, whereas two adjacent ribbons are connected via common corners. Further linkage results from the diphosphate groups, sharing each of the six equatorial oxygen atoms with adjacent octahedral ribbons. Using the modular description usually applied for the classification of cuspidine type structures the present compound belongs to the so called type 5 and is the first representative of this class.

INTRODUCTION

The crystal chemistry of apatites and related compounds are of interest because such compounds are used as additives in dental materials. Monofluorphosphate apatite is a promising candidate for investigation based on optical properties reported by Mehta and Simpson (1975). Hydrothermal synthesis at elevated pressures in sealed gold capsules (Mehta 1973; Mehta and Simpson 1975) provides quantities insufficient for dentistry. Our attempts to synthesize larger batches by solid state reaction under normal pressure yielded single crystals exhibiting optical properties identical to monofluorphosphate. However, the single-crystal structure analysis proved this phase to have diphosphate rather than monofluorphosphate groups. The compound, $Na_2Ca_2(P_2O_7)F_2$, belongs to a group of compounds named after the mineral cuspidine $Ca_4Si_2O_7(F,OH)_2$ (Saburi et al. 1977). All previously known cuspidine members were sorosilicates and the present phase is the first phosphate compound having the cuspidine-type structure. Our investigation confirms experimentally what Fleet and Pan (1995) proposed as the possible substitution of Ca^{2+} and Si^{4+} by Na^+ and P^{5+} in cuspidine type structures.

EXPERIMENTAL METHODS

$Na_2Ca_2(P_2O_7)F_2$ single crystals were obtained by heating mixtures of amorphous $NaPO_3$ and CaF_2 in stoichiometric proportions (3:2) in an anhydrous atmosphere of N_2 as well as O_2. The mixtures were heated between 693 K and 903 K for 12 hours each. Crystals suitable for single crystal structure investigations were obtained at 873 K. The diphosphate $Na_2Ca_2(P_2O_7)F_2$ represents about 90 wt% of the crystalline phases. Other phases were detected listed in order of decreasing abundance: fluorapatite $Ca_{10}(PO_4)_6F_2$, CaF_2, $Na_4P_2O_7$, and amorphous $NaPO_3$. The chemical composition of the single crystals was determined by electron microprobe analysis (Cameca SX50) with 15 kV accelerating voltage, 10 nA beam current, a defocused beam and a counting time of 20 s. The standards used for calibration were jadeite for Na, $CaSO_4$ for Ca, $AlPO_4$ for P, topaz for F. The results for two different crystals agree (Table 1) and represent an almost ideal stoichiometry.

Preliminary investigations of presumedly single crystals failed. All crystals exhibited platy morphology and normal optical behavior with sharp extinctions under the petrographic microscope. Precession photographs revealed orthorhombic Laue symmetry with lattice constants of about $a_o = 7.42$ Å, $b_o = 20.45$ Å, and $c_o = 10.54$ Å. The systematic absences indicated in the extinction symbol C-c- with the three possible space groups *Cmcm*, $Cmc2_1$, and $C2cm$. However, a structure determination using direct methods based on an intensity data set recorded with an Enraf Nonius CAD4 diffractometer failed. At this point twinning of the crystals was considered to explain the problems in the structure determination. The crystal used for the X-ray data collection was optically reinvestigated on a petrographic microscope equipped with a Medenbach spindle stage with internal refractometer. In this configuration, lamellar twinning was observed which did not appear when the crystal was viewed perpendicular to the plate. Consequently, this kind of twinning by pseudo-merohedry could not be detected in the preliminary studies. After, numerous samples were screened by single crystal film techniques, a crystal was found clearly deviating from orthorhombic symmetry. This indicates that the volume fraction of the single twin individuals significantly differs from 0.5, resulting in precession photographs showing the

* E-mail: rfischer@min.uni-bremen.de

TABLE 1. Results of the electron microprobe analyses

	Crystal A	Crystal B
Na_2O	18.09	18.10
CaO	33.48	33.29
P_2O_5	41.23	41.37
F	12.49	12.29
less O = F	5.26	5.18
Sum	100.03	99.87
	Formula per 7 O	
Na	2.030	2.021
Ca	2.077	2.066
P	2.021	2.017
F	2.286	2.239

true monoclinic symmetry. The metrical relationships between the false orthorhombic and the true monoclinic structure are described by $\mathbf{a}_m = (-\mathbf{a}_o + \mathbf{b}_o)/2$, $\mathbf{b}_m = \mathbf{c}_o$, $\mathbf{c}_m = \mathbf{a}_o$. Due to the exact superposition of the reciprocal lattices of the two monoclinic twin domains, splitting of the reflections cannot be observed. The systematic absences for $h\ 0\ l$ with $h + l = 2n + 1$ and $0k0$ with $k = 2n + 1$ resulted in space group $P12_1/n1$.

Data collection for the final structure analysis was performed on a Stoe IPDS single-crystal diffractometer using graphite monochromatized Mo$K\alpha$ radiation. The data were corrected for Lorentz and polarization effects. Details of the intensity measurements are given in Table 2. For structure solution the program SIR92 (Altomare et al. 1992) was used. Subsequent refinements were performed with the SHELXL-93 program (Sheldrick 1993). X-ray scattering factors for the different cations in their respective valence state together with anomalous dispersion correction were taken from the *International Tables of Crystallography Vol. C* (Wilson 1995); the values for O^{2-} were taken from Hovestreydt (1983). For drawing of structural details the programs STRUPLO90 (Fischer et al. 1991) and ORTEP-3 (Farrugia 1997) were used.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods. The phase set with the maximum combined figure of merit yielded a structure model with reasonable coordination spheres and interatomic distances. The refinement of atomic coordinates, anisotropic displacement parameters and constrained site occupancy factors of the cations converged at $R1 = 0.062$ and $wR2 = 0.1548$. Twinning was assumed although the precession photographs revealed a monoclinic Laue symmetry, indicating that the volume fractions of the two twin individuals differ significantly from 50%. There are two possibilities to convolute the two monoclinic $P2_1/n$ lattices to yield an orthorhombic C-centered lattice: a mirror plane parallel to the c-b-plane, $m_{(100)}$, or perpendicular to [001]. From X-ray and petrographic microscope investigations the lamallar twinning was observed with the (100) plane as composition plane. Introducing this plane as mirror plane as the element of twinning, the residuals $R1$ and $wR2$ dropped to 0.0493 and 0.1304, respectively; the value for the volume fraction α for twin component 1 refined to 9.2%.

As discussed below, the bridging oxygen atom O1 exhibits large vibrational displacement parameters, approximately perpendicular to the P-O-P bond of the diphosphate group. Therefore, the atom position O1 was split into two positions O1A and O1B. The displacement factor was isotropically constrained to be equal for the two atoms and the sum of the site occupancy factors of atoms O1A and O1B was constrained to the site occupancy of the general position. Final residuals converged at $R1 = 0.0431$ and $wR2 = 0.1142$. The refined atomic coordinates, equivalent isotropic and anisotropic displacement parameters, as well as selected interatomic distances and angles are given in Tables 3–6.

DESCRIPTION OF THE STRUCTURE

The structure is closely related to that of natural cuspidine and consists of ribbons of MX_6-octahedra (M = Na,Ca ; X = O,F) as the one of two main building unit running parallel **c**.The other main building unit are the diphosphate groups, which connect the octahedra ribbon.The real coordination of some cations is extended to sevenfold or eightfold-coordination. However, the inner coordination shell can be described as slightly distorted octahedra which simplifies the crystal chemical description.The octahedra of one ribbon are linked by edge-sharing. Two adjacent octahedral ribbons are connected via common corners. Furthermore, one diphosphate group links three adjoining ribbons. Figure 1 shows a projection of the ribbons and the phosphate tetrahedra parallel **c**. The cations Na^+ and Ca^{2+} can occupy four different positions, M1 to M4. Site occupancy refinements yielded M1: 0.83(1) Ca, 0.17(1) Na; M2: 0.45(1) Ca, 0.55(1) Na; M3: 0.54(1) Ca, Na 0.46(1) Na; M4 0.19(1) Ca, 0.81(1) Na. The positions M2 and M3 are the lateral centers of the ribbons. On these positions the cations Na and Ca are nearly equally distributed. The octahedral positions M1 and M4 inside the ribbon show a distinct preference for Ca^{2+} and Na^{+}, respectively. Sodium ions prefer the larger, more distorted $M4X_6$-, whereas calcium ions occupy almost completely the $M1X_6$-octahedra. Two groups of two polyhedra with

TABLE 2. Crystal cell data and experimental details for $Na_2Ca_2(P_2O_7)F_2$

a (Å)	10.8730(21)
b (Å)	10.5516(25)
c (Å)	7.4287(13)
β (°)	109.74(2)
V (Å^3)	802.2 (4)
Space group	$P\,2_1\,/\,n$
Z	4
Formula	$Na_2Ca_2(P_2O_7)F_2$
D_{calc} (g/cm^3)	2.80
μ (cm^{-1})	19.8
Crystal shape	fragment of a crystal plate
Diffractometer	Stoe-IPDS
Monochromator	Graphite
Rotation angle, no. of frames	2.0°, 130
Exposure time per frame	3 min
Θ-range	1.9–28.15°
Reflection range	$\lvert h \rvert \le 9$; $\lvert k \rvert \le 13$; $l \le 14$
No. of measured reflections	9884
No. of observed reflections [$I > 2\,\sigma(I)$]	4986
No. of unique reflections in *2/m*	1906
R_{int} for *2/m*	0.0637
variable parameters	141
$R1$ [$F_o > 4\,\sigma(F_o)$], $R1$ (all reflections)	0.0431, 0.0777
$wR2$ (all reflections)	0.1142
Weighting parameter *a, b*	0.062, 0.0
Goodness of Fit	0.985
Final $\Delta\rho_{min}$ (e/Å^3)	–0.89
Final $\Delta\rho_{max}$ (e/Å^3)	0.80
$R1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	$wR2 = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]^{0.5}$
$w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP]$	$P = [2F_c^2 + \max(F_o^2,0)] / 3$

TABLE 3. Positional parameters in fractional coordinates and equivalent isotropic displacement parameters (Å²)

Atom	number of atoms in unit cell	*x*	*y*	*z*	U_{eq}
M1	Ca: 3.30, Na: 0.70	0.5754(1)	0.8767(1)	0.6647(2)	0.0109(5)
M2	Ca: 1.81, Na: 2.19	0.8070(2)	0.1026(2)	0.5277(3)	0.0122(7)
M3	Ca: 2.14, Na: 1.86	0.8174(2)	0.0835(2)	0.0339(3)	0.0137(7)
M4	Ca: 0.75, Na: 3.25	0.5819(2)	0.8869(2)	0.1625(4)	0.0158(9)
P1	4	0.1241(1)	0.1832(2)	0.6435(2)	0.0075(4)
P2	4	0.6226(1)	0.3172(2)	0.7296(2)	0.0072(4)
F1	4	0.6126(4)	0.0022(3)	0.9231(6)	0.0140(8)
F2	4	0.6097(4)	0.0051(3)	0.4371(6)	0.0128(8)
O1	4	0.0929(12)	0.2002(7)	0.4216(12)	0.0999(40)
O2	4	0.8490(7)	0.9541(5)	0.7885(10)	0.0405(17)
O3	4	0.9975(5)	0.2320(5)	0.6535(11)	0.0390(18)
O4	4	0.1506(6)	0.0458(4)	0.6888(10)	0.0287(13)
O5	4	0.9977(5)	0.2300(5)	0.0903(10)	0.0420(20)
O6	4	0.7392(5)	0.2353(5)	0.7466(12)	0.0417(18)
O7	4	0.2399(5)	0.2659(5)	0.7412(11)	0.038(16)
O1A*		0.1670(15)	0.2114(13)	0.4546(25)	0.0284(15)
O1B*		0.0752(7)	0.1977(7)	0.4130(12)	0.0287(15)

Notes: U_{eq} = one third of the trace of the orthogonalized U_{ij} matrix. All atoms occupy Wyckoff site 4e.
* Position O1 may be split in to these.

TABLE 4. Anisotropic displacement parameters (Å² × 10⁴) for $Na_2Ca_2(P_2O_7)F_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M1	0.0127(8)	0.0105(7)	0.0098(9)	0.0009(6)	0.0043(6)	0.0034(6)
M2	0.0134(11)	0.0101(9)	0.0140(12)	–0.0008(7)	0.0058(8)	–0.0025(6)
M3	0.0138(10)	0.0135(9)	0.0146(11)	–0.0017(7)	0.0046(8)	–0.0039(6)
M4	0.0163(13)	0.0173(13)	0.0142(15)	0.0011(10)	0.0057(10)	0.0038(9)
P1	0.0083(8)	0.0075(7)	0.0073(9)	–0.0016(6)	0.0037(6)	0.0003(6)
P2	0.0072(7)	0.0066(7)	0.0078(9)	–0.0007(6)	0.0023(6)	–0.0002(6)
F1	0.0116(18)	0.0137(17)	0.0161(21)	–0.0027(18)	0.0039(17)	–0.0031(15)
F2	0.0108(21)	0.0130(17)	0.0151(18)	0.0008(15)	0.0052(16)	0.0017(18)
O1	0.2381(121)	0.0595(48)	0.0287(44)	0.0070(43)	0.0798(68)	0.0306(67)
O2	0.0779(45)	0.0117(27)	0.0353(40)	0.0028(26)	0.0235(34)	0.0147(28)
O3	0.0125(27)	0.0206(27)	0.0850(56)	–0.0253(31)	0.0178(30)	–0.0017(21)
O4	0.0409(31)	0.0108(24)	0.0385(37)	0.0074(24)	0.0188(28)	0.0065(23)
O5	0.0194(30)	0.0280(30)	0.0606(47)	0.0296(30)	–0.0100(28)	–0.0061(24)
O6	0.0110(27)	0.0252(28)	0.0833(52)	–0.0310(33)	0.0086(29)	0.0015(22)
O7	0.0137(28)	0.0246(28)	0.0648(45)	–0.0217(31)	–0.0020(28)	0.0022(22)

Notes: The anisotropic displacement factor exponent is defined as: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

different geometry can be distinguished. (1) The cations of the position M2 and M3 are coordinated octahedrally by six atoms within a sphere of 3 Å, of which five atoms are oxygen and one atom is fluorine. (2) In contrast to the M2- and M3-octahedra the coordination number of M1 and M4 are 7 and 8 up to 3 Å, respectively. Both cations at M1 and M4 are coordinated by three fluorine and four or five oxygen atoms. However, to a first approximation the $M1X_7$-polyhedron can be considered as an octahedron because the oxygen O2 of an adjoining ribbon has only a negligible contribution to the bond valence, 0.10 valence units (v.u.) for Ca^{2+} and 0.06 v.u. for Na^+ (Brown 1981) with a distance of 2.918 Å. The whole M1-coordination can be described as a monocapped octahedron.The coordination of the M4-position is more complex. Within the ribbon, M4 is octahedrally surrounded by 3 O and 3 F atoms. Furthermore, the oxygen atom O4 of the next octahedral ribbon and the bridging oxygen atom O1 of the diphosphate group belong to the coordination sphere. The whole M4-coordination can be described as a dicapped octahedron. Figure 2 shows the whole coordination of the M positions. The polyhedral representations of the structure with $M1X_7$- and $M4X_8$-polyhedra are simplified by reduction to octahedra.

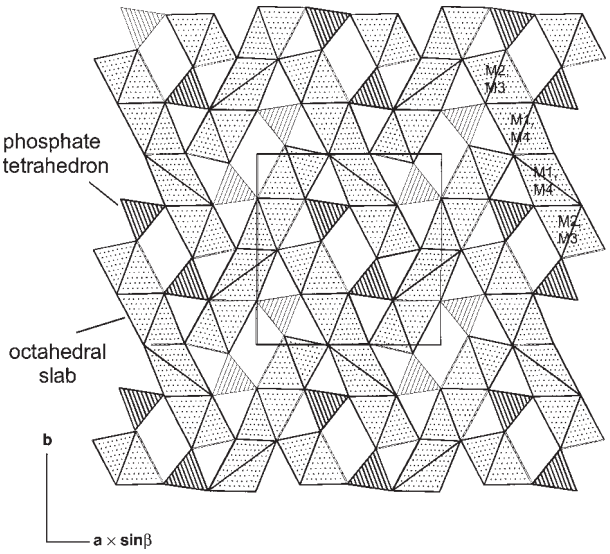

FIGURE 1. Projection (parallel [001]) of the octahedral ribbons linked by PO_4-tetrahedra.

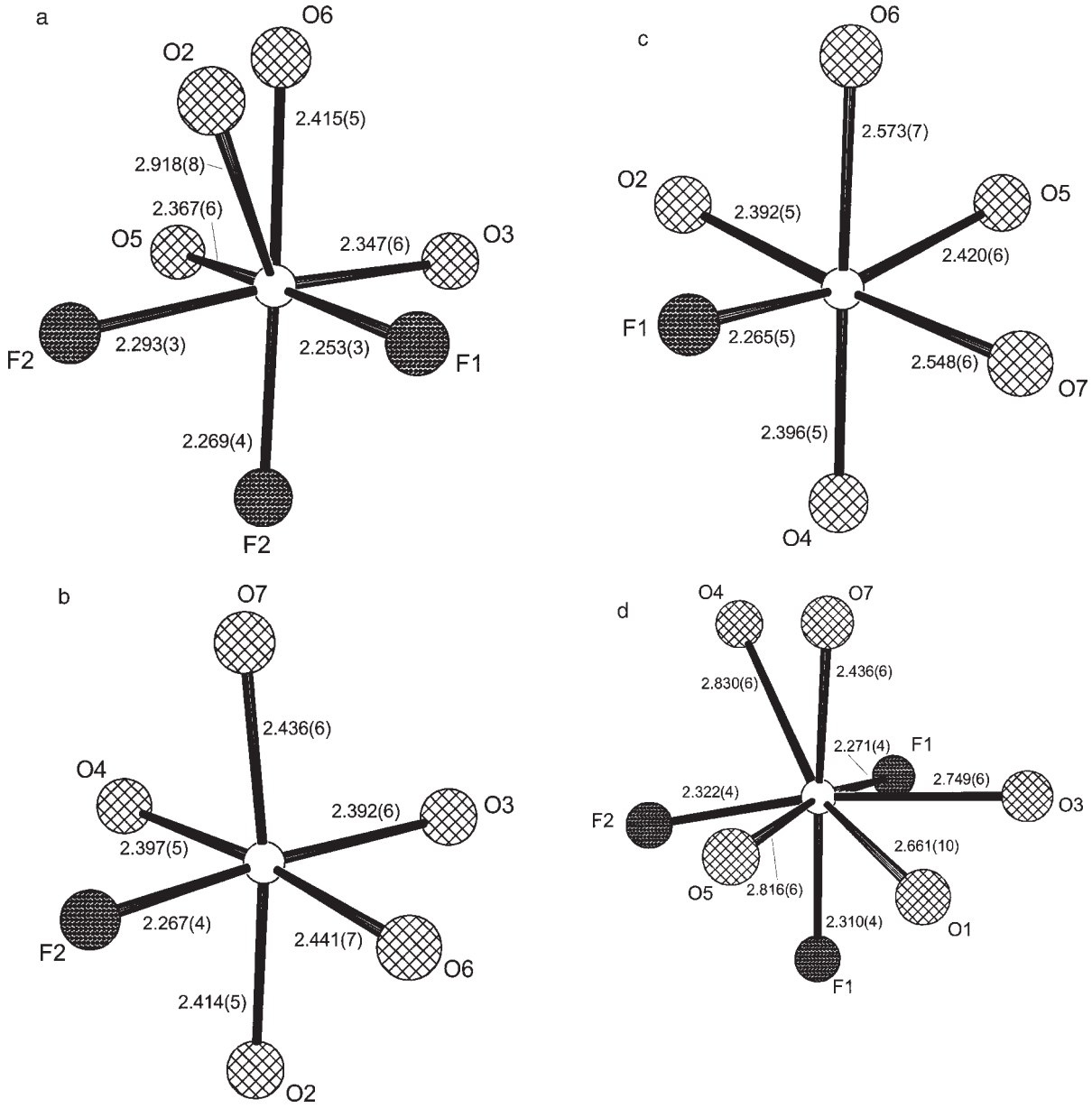

FIGURE 2. ORTEP3 (Farrugia 1997) drawings of M-polyhedra with bond distances (Å). The polyhedra are of (**a**) M1, (**b**) M2, (**c**) M3, and (**d**) M4.

Within the ribbon $M1X_6$- and $M4X_6$-octahedra as well as $M2X_6$- and $M3X_6$-octadedra alternate along the [001]-direction (Fig. 3). On the other hand, each fluorine atom is tetrahedrally coordinated by four M-cations.

The anion in the diphosphate groups has a P-O-P bond angle of 153.5(8)° (Table 6) with bridging P-O bond distances of 1.577(5) Å and 1.576(5) Å. The terminal P-O bonds have a mean length of 1.496 Å, while individual bond distances vary between 1.488 and 1.504 Å. The largest thermal displacements of the oxygen atoms O1, O3, O5, O6, O7 are nearly perpendicular to the P-O bond directions of the diphosphate groups (Fig. 4). The positional parameters from the structure refinement for these atoms correspond to an average position. Therefore, in subsequent refinements the position of the O1 atom was split into two positions O1A and O1B, resulting in final atom coordinates, isotropic displacement and site occupancy factors listed in Table 3. Furthermore, this model explains the large displacement factors of the oxygen atoms O3, O5, O6, and O7. The $P1O_4$- and $P2O_4$-tetrahedra slightly rotate about the P1-O4 and P2-O2 bonds, respectively, to permit occupation of position O1A or O1B by the bridging oxygen atom O1. The direction of rotation from the average position is indicated by arrows in Figure 4.

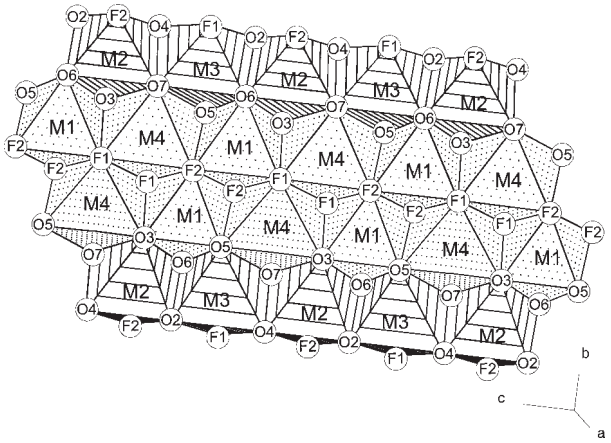

FIGURE 3. Side view of the octahedral ribbon.

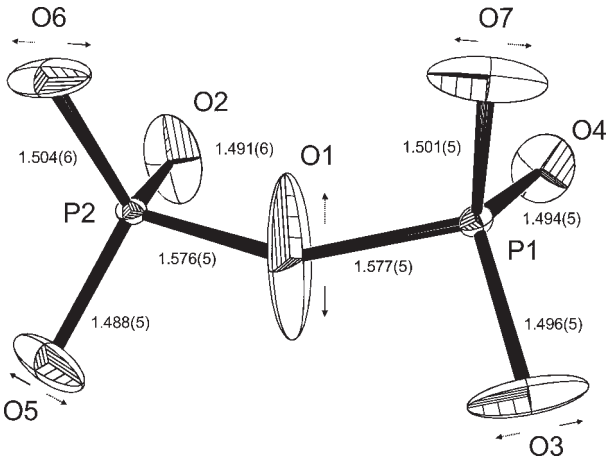

FIGURE 4. The model of the diphosphate ion with anisotropic displacements [50% probability displacement ellipsoids and bond distances (Å)] plotted with program ORTEP3 (Farrugia 1997).

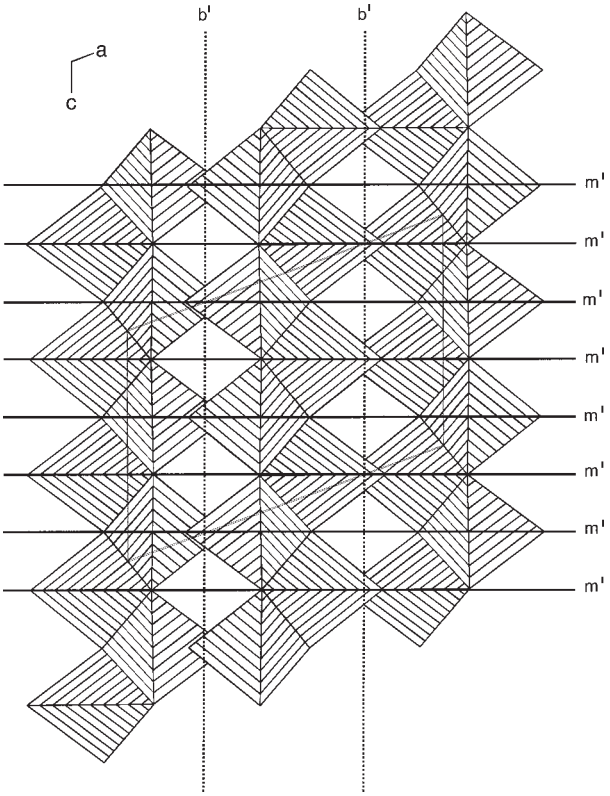

FIGURE 5. Schematic polyhedral view of the FM4-substructure parallel [010] with possible twin planes m' ⊥ **c** and b' glide plan parallel (100).

Bond valences were calculated for the diphosphate group for a structure model with and without a split position for the bridging oxygen atom O1 (Table 7). Without splitting, the negative valence for the O1-atom is 13% higher than the normal –2 value. A split position leads to a difference in bond valence from the theoretical value of 2 valence units of about 1.0% for the oxygen atom O1A and 0.5% for the oxygen atom O1B. The bond valence calculation supports the assumption of a disorder of the diphosphate group. In related cuspidine structures with different cation types, for example hiortdahlite II (Merlino and Perchiazzi 1987) and $NaCa_2LuSi_2O_7F_2$ (Fleet and Pan 1995), a slight disorder of the disilicate groups was also observed. However, in the present work the oxygen atoms of the diphosphate group show higher displacements from an average position. Because the dimension of the octahedral ribbon is similar to cuspidine group structures and the bond length in the diphosphate groups is shorter than in disilicate groups, the shift from the average position must be larger for the same compensation of valence.

TABLE 5. Selected interatomic distances (Å)

P1-O4	1.494(5)	P2-O5	1.488(5)
P1-O3	1.495(5)	P2-O2	1.493(5)
P1-O7	1.502(5)	P2-O6	1.504(5)
P1-O1	1.577(9)	P2-O1	1.576(9)
Mean	1.517	Mean	1.515
M1-F1	2.253(4)	M3-F1	2.266(4)
M1-F2	2.269(4)	M3-O2	2.394(7)
M1-F2,	2.293(4)	M3-O4	2.396(6)
M1-03	2.347(6)	M3-O5	2.419(6)
M1-O5	2.366(6)	M3-O7	2.546(8)
M1-O6	2.414(5)	M3-O6	2.573(8)
M1-O2	2.918(8)		
Mean	2.409	Mean	2.432
M2-F2	2.267(4)	M4-F1	2.271(5)
M2-O3	2.392(5)	M4-F1'	2.310(5)
M2-O4	2.398(6)	M4-F2	2.322(5)
M2-O2	2.413(7)	M4-O7	2.435(6)
M2-O7	2.437(7)	M4-O1	2.661(10)
M2-O6	2.441(7)	M4-O3	2.749(8)
Mean	2.391	M4-O5	2.817(8)
		M4-O4	2.831(6)
		Mean	2.550

TABLE 6. Selected bond angles (°)

O1-P1-O3	97.8(5)	O1-P2-O5	99.9(5)
O1-P1-O4	107.6(4)	O1-P2-O2	107.8(4)
O1-P1-O7	106.8(5)	O1-P2-O6	106.4(5)
O7-P1-O3	114.3(3)	O6-P2-O5	114.3(3)
O7-P1-O4	112.9(3)	O6-P2-O2	111.7(4)
O4-P1-O3	115.7(3)	O2-P2-O5	115.4(4)
Mean	109.2	Mean	109.2

Notes: P1-O1-P2 the angle is 153.5(8).

Twinning is usually related to structural features frequently resulting from pseudo-symmetry elements which superimpose the atoms of a partial structure onto each other. In $Ca_2Na_2(P_2O_7)F_2$, this observation can be easily verified from Figure 5, where the substructure of the FM_4-tetrahedra is shown. Two systems of pseudo symmetry elements being perpendicular to each other exist: (1) mirror planes *m*' and (2) *b*'-glide planes. Both pseudo symmetry elements could explain the twinning. However, from the orientation of the macroscopic twin planes observed in the optical investigations only the pseudo *b*'-glide plane is responsible for the twinning.

Diffuse effects which could indicate structural disorder were not observed in the precession photographs and the image plate recording of the single crystal diffractometer. However, it has been pointed out by Merlino (private communication) that the structure could be described on the basis of order-disorder effects (OD-theory) similar to the mineral burpalite (Merlino et al. 1990).

COMPARISON WITH RELATED STRUCTURES

$Na_2Ca_2(P_2O_7)F_2$ is the first example of a cuspidine type compound with diphosphate instead of disilicate groups. The silicate members of the cuspidine group (cuspidine, wöhlerite, niocalite, lavenite, hiortdahlite, janhaugite, baghadite, synthetic $NaCa_2Lu(Si_2O_7)F_2$) and the compound investigated here show the same main building units: (1) four octahedral ribbons, four columns wide, parallel to [001] and (2) T_2O_7 groups, interconnecting the ribbons via common corners. Merlino and Perchiazzi (1988) summarized these structural features and developed a description with ten different structure types based on four different unit-cell types, and different relative height of T_20_7 groups paralllel to [001]. $Na_2Ca_2(P_2O_7)F_2$ is the first member which corresponds to topology structure type 5 proposed by these authors: P_2O_7 groups linked to adjacent columns differ in height by about *c*/4 and P_2O_7 groups linked to the same column on opposite of the wall differ in height by about *c*/2.

ACKNOWLEDGMENTS

Financial support for this work has been received from the Deutsche Forschungsgemeinschaft. We thank G. Roth (RWTH Aachen) for the data collection, H.-J. Bernard (Universität Bochum) for the electron microprobe analysis, and H. Effenberger (Universität Wien) and S. Merlino (Università di Pisa) for their careful reviews and suggestions.

TABLE 7. Bond valence calculation for the bridging oxygen atom of the diphosphate group

Atom 1	Atom 2	Distance (Å)	Bond valence *s* (v.u.)
	Structure without O1 split position		
O1	P1	1.577	1.13
	P2	1.576	1.13
			Σ = 2.26
	Structure with O1 split position		
		(Å)	Valence s (v.u.)
O1A	P1	1.648	0.93
	P2	1.604	1.05
			Σ = 1.98
O1B	P1	1.620	1.00
	P2	1.618	1.01
			Σ = 2.01

Notes: After Brown (1981) according to $s = \exp[-(R-R_0)/B]$, *R*: calculated bond distance, $R_0 = 1.62$, $B = 0.36$.

REFERENCES CITED

Altomare, A., Cascarano, C., Giacovazzo, G., Guagliardi, A., Burla, M.C., Polidori, G., and Camalli, M. (1992) SIR92:A program for automatic solution of structures by direct methods. Journal of Applied Crystallography, 27, 435.

Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical structure and bonding. In O'Keeffe and A.Navrotsky, Eds., Structure and bonding in crystals II, p. 1–30. Academic Press, New York.

Farrugia, L.J. (1997) ORTEP-3 for windows: a version of Ortep III with graphical user interface (GUI). Journal of Applied Crystallography, 30, 565.

Fischer, R.X., LeLirzin, A., Kassner, D., and Rüdinger, B. (1991) STRUPLO90, eine neue Version des Fortranprogramms zur Darstellung von Kristallstrukturen. Zeitschrift für Kristallographie, Supplemental Issue, 3, 75.

Fleet, M.E. and Pan, Y. (1995) The structure of $NaCa_2LuSi_2O_7F_2$, a synthetic phase of the cuspidine group. Canadian Mineralogist, 33, 879–884.

Hovestreydt, E. (1983) On the atomic scattering factor of O^{2-}. Acta Crystallographica, A39, 268–269.

Mehta, S. (1973) Sulfate and monoflorophosphate bearing apatite. PhD thesis, Lehigh University, Pennsylvania.

Mehta, S. and Simpson, D.R. (1975) Fluoride in apatite: substitution of monofluorophosphate for orthophosphate. American Mineralogist, 60, 134–138.

Merlino, S. and Perchiazzi, N. (1987) The crystal structure of hiortdahlite II. Mineralogy and Petrology, 37, 25–35.

———(1988) Modular mineralogy in the cuspidine group of minerals. Canadian Mineralogist, 26, 933–943.

Merlino, S., Perchiazzi, N., Khomyakhov, A.P., Pushcharovskii, D.Y., Kulikova, I.M., and Kuzmin, V.I. (1990) Burpalite, a new mineral from Burpalinskii massif, North Transbajkal, USSR: ist crystal structure and OD character. European Journal of Mineralogy, 2, 177–185.

Saburi, S., Kawahara, A., Henmi, C., Kusachi, I., and Kihara, K. (1977) The refinement of the crystal structure of cuspidine. Mineralogical Journal, 8, 286–298.

Sheldrick, G.M. (1993) SHELXL-93. Program for the refinement of crystal structures. Universität Göttingen, Germany.

Wilson, A.J.C., Eds. (1995) International tables for crystallography, Volume C. Kluwer, Dordrecht, Netherland.

MANUSCRIPT RECEIVED NOVEMBER 23, 1999
MANUSCRIPT ACCEPTED APRIL 30, 2000
PAPER HANDLED BY GERALD GIESTER