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Synthesis and Crystal Structure of a Tubular Hydroxyphosphite: $Zn_{11}\square(HPO_3)_8(OH)_6$

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$Zn_{11}\square(HPO_3)_8(OH)_6$ is hexagonal, space group $P6_3mc$, $Z = 1$, $a = 12.872(1)$ Å, $c = 4.9772(4)$ Å; $R = 0.030$ for 986 reflections from single-crystal X-ray diffraction data. This compound is unexpectedly isotypical with $A_3Te_2O_6(OH)_2$ (A = Co, Ni) and related to that of dumortierite. It is built up from zigzag (pyroxene-like) octahedra-edge-shared chains which fuse by face-sharing to form double chains. Connection of these double chains by corner sharing of octahedra builds an open tridimensional framework delimiting two kinds of channels running parallel to c. The smaller channels are occupied by 2/8 of the HPO_3 groups. On the walls of the largest tunnels are connected the remaining HPO_3 groups, with their hydrogen atoms pointing toward the tunnel center, forming an unusual infinite chain of empty $[H_6]$ octahedra sharing faces along the c axis. Comparison with the tellurates and the dumortierite structures is given. © 1993 Academic Press, Inc.

Introduction

The crystal chemistry of inorganic phosphites was recently reviewed and systematized (*1, 2*). The total number of known compounds remains small. Among phosphites with a P:O ratio of 1:3 the most representative are those including $H_2PO_3^-$ (type *C*) and HPO_3^{2-} (type *E*) anions with, respectively, 12 and 16 detailed structure analyses (*2*). We have increased this family by the structure determination and magnetic study of $CoHPO_3 \cdot H_2O$ (*3*) and the structure determination of a hypophosphite $[CoCl(H_2PO_2)] \cdot H_2O$ presenting a layer structure (*4*).

This paper describes the synthesis and structure determination of $Zn_{11}\square(HPO_3)_8(OH)_6$, showing an unexpected relationship with some silicate and tellurate compounds. As emphasized in (*5*), phosphites lead frequently to noncentrosymmetric structures due to the C_{3v} local symmetry of the HPO_3 group. This is verified for $Zn_{11}\square(HPO_3)_8(OH)_6$; it was also the case for $CoHPO_3 \cdot H_2O$ (*3*).

Experimental

The Synthesis of $Zn_{11}\square(HPO_3)_8(OH)_6$ was carried out using hydrothermal conditions. $ZnCl_2 \cdot 2H_2O$ (2.292 g) was dissolved in 10 cm^3 of water and the pH was adjusted to 7 with NaOH solution. Then 4 cm^3 of H_3PO_3 were added over the suspension with stirring; 15 cm^3 of this suspension were introduced in a hermetic teflon bucket and placed in a metallic container heated at 180°C for 48 hr. It was cooled down to room temperature for 24 hr. Translucent crystals mixed with an amorphous material were obtained. Crystals were separated and washed with small portions of acetone. The composition was determined from the structure analysis.

Structure Determination

A needle with a hexagonal section was selected for the structure determination. The data were collected on a Siemens AED2 four-circle diffractometer. Table I gathers the experimental conditions. The parame-

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TABLE I

CRYSTALLOGRAPHIC DATA FOR $Zn_{11}\square(HPO_3)_8(OH)_6$

Space group	$P6_3mc$
Z	1
Molecular weight	1461.1
Calculated density	3.397
Radiation	Mo $K\alpha$
μ (cm^{-1}), Mo $K\alpha$	98.7
Crystal dimensions (mm)	0.04 × 0.04 × 0.11
Lattice constants (Å)	
a	12.872(1)
c	4.9772(4)
Volume ($Å^3$)	714.2
Scan type	ω-2θ
T	20°C
Angular range (°2θ)	3.7–70.0
Learn profile data collection	
Isotropic line width (°) A	0.7566
$\omega = (A + B \text{ tg } \theta)°$ B	0.2739
Maximum h,k,l	17,11,8
Data examined	1346
Unique reflections	1121 $R_{av} = 0.016$
Merged data retained	986 $I > 3\ \sigma(I)$
Absorption correction	Gauss method
Min and max transmission	0.4781 0.5303
Refinement	
R	0.030
R_w	0.036
Weight: $k/(\sigma^2(F) + GxF^2)$	
k	2.6414
G	0.00013
Extinction parameter	$1.1(3) \times 10^{-7}$
No. of variables	53
Max shift/esd	0.002
Max and min electron density in final Fourier difference map ($e \cdot Å^{-3}$)	4.05, −1.55

ters of the hexagonal cell were refined from 42 reflections well distributed in the reciprocal space near 30°(2θ). The Laue group was 6/*mmm* and the conditions limiting possible reflections were consistent with the $P6_3/mmc$, $P\bar{6}2c$, *and* $P6_3mc$ space groups. All calculations were made with the SHELX-76 program (*6*). Atomic scattering factors and anomalous dispersion correction terms were taken from the "International Tables for X-Ray-Crystallography" (*7*).

Although the final structure is described using the noncentrosymmetric $P6_3mc$ space group, the E statistic was not clearly in favor of either the absence or the presence of an inversion center ($\langle E^2 - 1 \rangle = 0.835$). Thus we tried first to determine the structure using the $P6_3/mmc$ space group. A starting set of coordinates, with Zn on a 12*j* site and P on a 6*h* site, was obtained using the Patterson method. Refinements of these coordinates led to $R = 0.23$. Fourier difference syntheses did not allow us to complete the structure; the possible sites were related by pairs at too close a distance. Thus we turned toward the two possible noncentrosymmetric space groups. The final results were obtained by using the $P6_3mc$ space group with a structure organization which could not be described by using the $P\bar{6}2c$ space group. The Zn and P atoms, previously obtained in the $P6_3/mmc$ space group, were easily placed, respectively, on a general position and a 6*c* site in the $P6_3mc$ space group. The origin along the *c* axis was chosen by fixing the *z* coordinate of the Zn atom to zero. Then successive atoms were placed one by one with some difficulties because the Fourier difference map always indicated an alternative site for each atom (related by x, y, $\pm z$ coordinates). When all nonhydrogen atoms were placed, the R factor decreased to 0.050 using isotropic thermal motion approximation. Changing all coordinate signs led to $R = 0.066$, giving a confirmation of the absolute configuration choice. When using anisotropic thermal motion parameters, the R factor decreased to 0.034. At this stage, the formula was estimated as being "$Zn_{12}(PO_3)_8O_6$." The presence of HPO_3 groups were consequently probable, in agreement with the method of synthesis. Hydrogen atoms corresponding to these HPO_3 groups were located from a Fourier difference synthesis using data limited to $\sin \theta < 0.4$, indicating also another hydrogen atom site leading again to a nonequilibrated formula "$Zn_{12}(HPO_3)_8(OH)_6$."

Afterward, we considered three possible formulae which could satisfy electrical neutrality, $Na_2Zn_{10}(HPO_3)_8(OH)_6$, $Zn_{12}(HPO_3)_8(O,OH)_6$, or $Zn_{11}\square(HPO_3)_8(OH)_6$ with a zinc atom vacancy. The first

proposition was suggested by the presence of NaOH during the synthesis and could be supported by crystal chemistry arguments as explained at the end of the Discussion. However, it was ruled out by EDX analysis pointing out the Na absence. The third proposition was supported against the second one by the abnormally high thermal motion of the zinc atom; a refinement of the Zn atom occupancy factor led to 0.912(7), a value very close to the expected one (0.917) for an exact 11 : 12 occupancy (the Zn atom thermal motion and occupancy factor were refined simultaneously, the corresponding correlation matrix elements being smaller than 0.5; the correlation between the scale factor and the Zn atom occupancy was −0.72, as obtained from the SHELX-76 program). This result was believed to be conclusive for the existence of a zinc atom vacancy. A strict 11/12 occupancy was fixed in further refinements. No supercell could be detected from prolongated exposures using photographic X-ray diffraction methods. Refinement of hydrogen atom coordinates was realized by using some constraints on distances. The P–H bond lengths corresponding to the two independent P atoms were constrained to have the same value within ±0.01 Å, this value being refined. In the case of the H atom of the hydroxyl group, the O–H distance was constrained to be 0.90 ± 0.01 Å. The final R factors are listed in Table 1 together with other details of the measurement and refinement. It must be emphasized that the large residual peak (4.05 $e \cdot Å^{-3}$) quoted Table I was observed on the final Fourier difference map at 0.4 Å from the zinc atom site. In case of disordered structures, it is generally difficult to decide when to stop refinements. It was reasonable to stop at this stage, however we can indicate that the R value could be decreased to 0.022, taking account for this suggested splitting of the zinc atom site without any significant change on all other parameters. The splitting could correspond to some local effect due to the zinc atom vacancy. Each oxygen atom has two zinc atom neighbors in this structure, so when a zinc atom is lacking, the oxygen atom charge deficit must be compensated by a locally shorter Zn–O distance involving the remaining zinc atom. This could be obtained by displacement of either the oxygen or the zinc atoms. Maybe we have the indication that this is accomplished mainly by displacements of Zn atoms.

The absolute configuration choice limited above to a simple comparison between two R values was checked by the Flack method (*8*), using a program able to treat inversion-twinned crystals (*9*) and to refine the so-called enantiomorph-polarity parameter x, defined by $F^2(hkl, x) = (1 - x)\, F^2(hkl) + x\, F^2(\overline{hkl})$. First, a global scale factor was refined, together with all other parameters, leading to $R_F = 0.039$, x being fixed to 0.5. Then, the scale factor was kept fixed whereas x was refined with other parameters converging well in a few cycles to $x = 0.18(1)$, corresponding to $R_F = 0.032$. This would suggest some inversion-twinning degree. In fact, refining independently two scale factors, one for each domain of this hypothetically inversion-twinned crystal, starting from a ratio deduced from the above x value, led to a lower R_F (0.030) and to one of the scale factors tending toward zero. So, finally, the crystal is probably untwinned. By using the SHELX-76 program, the $R = 0.053$ and $R_W = 0.061$ of a refinement with -(xyz) coordinates and anisotropic thermal parameters were quite distinct from those quoted Table I corresponding to the final refinement with (xyz) coordinates.

Atomic coordinates and temperature factors are listed in Table II. Selected bond lengths and angles are gathered in Table III. A list of observed and calculated structure factors may be obtained on request to the authors.

Description of the Structure and Discussion

A projection along [001] of the crystal structure of $Zn_{11}\square(HPO_3)_8(OH)_6$ is shown

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS ($U_{ij} \times 10^4$) FOR $Zn_{11}\square(HPO_3)_8(OH)_6$

Atom	Site	x	y	z	B_{eq} (Å^2)
Zn[a]	12*d*	0.42918(4)	0.34856(4)	0.0	1.47(2)
P(1)	6*c*	0.16139(5)	$-x$	0.9810(3)	1.01(4)
P(2)	2*b*	2/3	1/3	0.7538(5)	0.88(5)
O(1)	12*d*	0.3437(2)	0.0736(2)	0.6437(5)	1.4(1)
O(2)	6*c*	0.1981(2)	$-x$	0.7180(7)	1.5(2)
O(3)	6*c*	0.3987(2)	$-x$	0.339(1)	2.0(2)
O(4)	6*c*	0.4747(1)	$-x$	0.8018(7)	1.3(2)
H(1)	6*c*	0.449(3)	$-x$	0.94(1)	2.3(9)[b]
H(2)	6*c*	0.099(4)	$-x$	0.93(1)	2.3(9)[b]
H(3)	2*b*	2/3	1/3	0.47(1)	2.3(9)[b]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	190(2)	205(2)	157(2)	−29(2)	−20(2)	93(1)
P(1)	123(3)	U_{11}	122(5)	0(2)	$-U_{23}$	50(3)
P(2)	92(4)	U_{11}	152(8)	0	0	46(2)
O(1)	245(11)	149(9)	131(9)	19(8)	−5(9)	102(8)
O(2)	188(10)	U_{11}	130(13)	−54(7)	$-U_{23}$	47(12)
O(3)	134(10)	U_{11}	487(26)	11(8)	$-U_{23}$	69(12)
O(4)	187(10)	U_{11}	145(14)	−20(6)	$-U_{23}$	112(13)

Note. Vibrational U_{ij} coefficients relate to the expression $T = \exp[-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

[a] Occupancy factor 11/12.

[b] B(Å^2), one value for all H atoms.

in Fig. 1. The complex framework of this compound is controlled by the packing of all the zinc and oxygen atoms forming $[ZnO_6]$ octahedra. Each octahedron shares an edge with two others $[ZnO_6]$ octahedra at $z \pm 1/2$ resulting in an infinite zig-zag pyroxene-like chain of $(ZnO_4)_n$ formula (not taking account for the vacancy). Also each $[ZnO_6]$ octahedron of these single chains shares a face with another one at the same z level. In this way, two single chains fuse to form a $[Zn_4O_{11}]_n$ double chain running along the c direction. Connection of the double chains by corner sharing of octahedra builds an open tridimensional framework delimiting two kinds of channels running along the c axis. The smaller channels, of triangular section, are occupied by 2/8 of the HPO_3 groups (having $3m$ symmetry). The six remaining HPO_3 groups (with m symmetry) are located on the walls of the largest hexagonal channels, with their hydrogen atoms pointing toward the tunnel center. In this way are generated unusual infinite chains of empty $[H_6]$ face-sharing octahedra running parallel to c. The distance between the unoccupied gravity center of these octahedra and the H(2) hydrogen atoms is 2.53 Å, the shortest H(2)–H(2) distance being 3.33 Å. This cavity seems to be slightly too small to accept the insertion of a water molecule.

About distances, they compare well with literature data. The $[ZnO_6]$ octahedron shows a notable distortion mainly due to O(4) which belongs to an hydroxyl group and is shared by four zinc atoms. One of the Zn–O(4) distances (Table III) is quite long (2.270 Å); the others vary in a short range of values (2.065–2.139 Å). The latter short distances are similar to those reported

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $Zn_{11}\square(HPO_3)_8(OH)_6$

Zn Octahedron ⟨Zn–O⟩ = 2.129

	O(1)	O(2)	O(4)	O(3)	O(1)	O(4)
O(1)	**2.065(2)**	3.180(3)	4.119(1)	3.030(3)	2.980(3)	2.950(2)
O(2)	100.6(2)	**2.069(2)**	3.111(2)	3.220(3)	3.052(1)	4.333(2)
O(4)	162.9(1)	96.5(2)	**2.100(2)**	2.859(5)	2.950(2)	2.732(4)
O(3)	92.5(2)	100.2(2)	85.1(3)	**2.129(3)**	4.235(4)	2.826(1)
O(1)	90.3(2)	93.0(2)	88.2(2)	165.8(2)	**2.139(2)**	3.022(3)
O(4)	85.6(2)	173.8(1)	77.3(3)	79.9(2)	86.5(2)	**2.270(1)**

P(1) Tetrahedron ⟨P–O⟩ = 1.527

	H(2)	O(1)	O(1)	O(2)
H(2)	**1.41(6)**[a]	2.32(6)	2.32(6)	2.45(2)
O(1)	104(2)	**1.519(2)**	2.527(2)	2.535(2)
O(1)	104(2)	112.6(2)	**1.519(2)**	2.535(3)
O(2)	112(1)	111.8(2)	111.8(2)	**1.544(3)**

P(2) Tetrahedron ⟨P–O⟩ = 1.517

	H(3)	O(3)	O(3)	O(3)
H(3)	**1.41(6)**[a]	2.35(3)	2.35(3)	2.35(3)
O(3)	106(3)	**1.517(2)**	2.522(3)	2.522(4)
O(3)	106(3)	112.5(2)	**1.517(2)**	2.522(4)
O(3)	106(3)	112.5(2)	112.5(2)	**1.517(2)**

Hydrogen bonding O(4)–H(1) 0.90[b]

H(1)···O(3) 2.28(5)	O(4)–O(3) 3.165(3)	O(3)–H(1)–O(4) 170(4)
H(1)···O(4) 2.48(8)	O(4)–O(4) 2.732(4)	O(4)–H(1)–O(4) 97(3)

Octahedra sharing

Face	Edge	Corner
Zn–Zn 2.861(1)	Zn–Zn 2 × 3.070(1)	Zn–Zn 3.449(1)
		Zn–Zn 2 × 4.196(1)

[a] Values constrained to be equal.
[b] Fixed value.

for related compounds as $Zn(H_2PO_2)_2(H_2O)_n$ (n = 0, 1) (*10*), $Zn(H_2PO_3)_2(H_2O)_3$, $Zn_2(HPO_3)_2(H_2O)_5$, $Zn_3A_2(HPO_3)_4$ (A = Na, K), $Zn_3Ba(HPO_3)_4(H_2O)_6$ (*11*), and $ZnB(HPO_3)_2(H_2O)_2$ (B = Ca, Sr) (*12*). It was emphasized in (*11*) that phosphite hydrogen atoms behave as "dead ends" in propagating the frameworks, so phosphite structures tend to have open cavities. The large circular cavities running parallel to c in $Zn(H_2PO_3)_2(H_2O)_3$, although lined by both terminal OH and H groups of the phosphite anions, show some analogies with the tunnels of the title compound. Along the tunnels, isolated [H_6] octahedra alternate with larger cavities in $Zn(H_2PO_3)_2(H_2O)_3$. The size of these [H_6] octahedra is larger than those of the title compound, the usable radius being 3.27 Å. However, the water molecules, which are likely present in this structure, were not located. They were believed to be bonded to the terminal P–OH groups in a disordered way.

For $Zn_{11}\square(HPO_3)_8(OH)_6$, in spite of the disorder induced by the zinc atom vacancy, a bond valence analysis carried out using the Zachariasen law (*13*) (see Table IV) leads to the expected valences within 10% error (without correcting for the Zn atom occupancy). The identification of O(4) as belong-

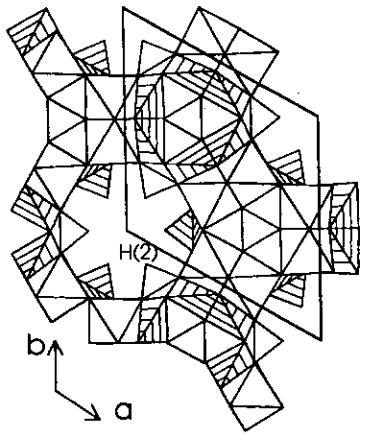

FIG. 1. View of the structure of $Zn_{11}\square(HPO_3)_8(OH)_6$ along [001]. The distinctly dashed [ZnO_6] octahedra and [HPO_3] tetrahedra are at different z levels (zinc atoms at $z = 0$ and $z = 1/2$).

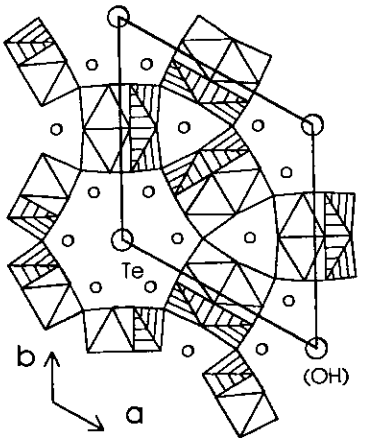

FIG. 2. View of the structure of $Co_3Te_2O_6(OH)_2$ along [001]. The distinctly dashed [CoO_6] octahedra are at different z levels. Large circles correspond to (OH) groups, small circles to Te atoms.

ing to an hydroxyl group is confirmed. From the long H(1)···O distances, it may be concluded that the bond is weak and may be bifurcated, involving O(3) and O(4) (Table III). A total bond valence near of 4 is obtained for both P atom sites (to be attributed in fact to HP^{4+}).

Searching possible related materials by using the Inorganic Crystal Structure Database, (ICSD (*15*)), an unexpected similitude with the hydroxytellurites $M_3Te_2O_6(OH)_2$ (M = Co, Ni) (*16*) was established (same space group and similar parameters: $a \approx 13$ Å and $c \approx 5$ Å). In these latter compounds (see Fig. 2), the complex tridimensional network of [MO_6] octahedra sharing corners, edges and faces is basically the same as that built from [ZnO_6] octahedra in $Zn_{11}\square(HPO_3)_8(OH)_6$. In both structures, pseudotetrahedra (HPO_3 or $ETeO_3$, E = lone pair) delimit infinite chains of [H_6] and [E_6] face-sharing octahedra running along the c axis. These octahedra are empty in the title compound and were suggested to be fully occupied by probably two hydroxyl groups in the tellurates. Hydrogen atoms were not located in Ref. (*16*); eight per cell were necessary for an equilibrated formula. The presence of D for a deuterated sample was established from IR measurements. Performing a valence bond analysis from the tellurates structural data, we have verified the probable presence of six hydroxyl groups in the position analogous to that of O(4) in the phosphite. There are two remaining noticeable differences between these structures: the positions of Te and P (in the 2*b* site) according to the basal oxygen triangle are opposite (up and down) and the configurations allowed by the noncentrosymmetrical space group are inverse (how-

TABLE IV

VALENCE BOND ANALYSIS FOR $Zn_{11}\square(HPO_3)_8(OH)_6$ USING THE ZACHARIASEN LAW

	Zn	HP(1)	HP(2)	Σ
O(1)	0.37	1.32		1.92
	0.30	×2		
O(2)	0.36 × 2	1.23		1.95
O(3)	0.31 × 2		1.33	1.95
			×3	
O(4)	0.33 × 2			1.10
	0.22 × 2			
Σ	1.89	3.87	3.99	

Note. $s = \exp[-(R - R_0)/B]$; $R_0 = 1.675$ and $B = 0.39$ for Zn and 1.620 and 0.36 for P (*14*).

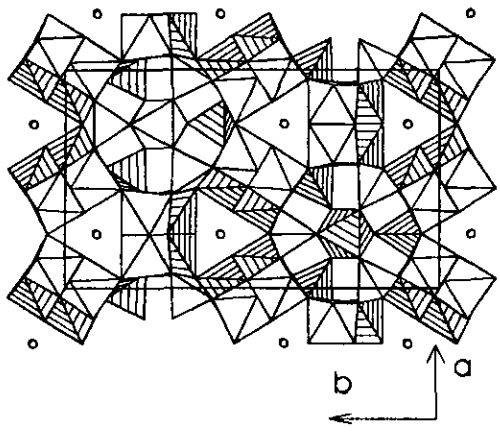

FIG. 3. View of the dumortierite structure. Small circles correspond to B atoms.

ever, there was no mention of an absolute configuration test in the tellurates study). Relation between compounds based on HPO_3 and $ETeO_3$ tetrahedra have been yet previously noted for $CuHPO_3 \cdot 2H_2O$ (*17, 18*) and $CuTeO_3 \cdot 2H_2O$ (*19*); the relation applies also to isotypical $CuSeO_3 \cdot 2H_2O$ (*20*).

Another related compound with very similar structure is the dumortierite natural mineral. The structure of this complex oxyborosilicate of aluminum was determined by Golovastikov (*21*) and revisited by Moore and Araki (*22*), who performed a quite detailed structure analysis. The cell is orthorhombic with *a*, *b*, and *c* parameters respectively near the *a*, $a\sqrt{3}$, and *c* parameters of the phosphite. There are three kinds of chains in dumortierite, each built up from $[AlO_6]$ octahedra (see Fig. 3). The first type is based on an infinite chain of face-sharing octahedra, with Al–Al separations of only $c/2 = 2.35$ Å. Such chains are in fact partly disordered with Al occupancy factors ranging from 0.84 to 0.93 (*23*), they are analogous to the infinite chains of empty $[H_6]$ octahedra in our phosphite or to those ($[E_6]$) occupied by OH groups in the tellurate compounds. The second type of chain in dumortierite is based on the zigzag (pyroxene-like) edge-shared chain which fuses by face sharing to an equivalent chain to form a double-chain of composition $[Al_4O_{12}]$. In $Zn_{11}\square(HPO_3)_8(OH)_6$, the framework of ZnO_6 octahedra is built up exclusively by such double chains connected by corners and delimiting the same triangles and hexagons present in dumortierite. According to Moore and Araki (*22*), these first two types of chains correspond to sections of hexagonal close packing. The third type of chains does not exist in the zinc phosphite or in the tellurate phases but only in the dumortierite, where it is a section of cubic close packing and has also the composition $[Al_4O_{12}]$ with corner and edge sharing between $[AlO_6]$ octahedra but no face sharing. Moore and Araki (*22*) considered the feasibility of building polymorphs of the dumortierite and proposed that an hypothetical $P6_3mc$ phase could exist showing only the first and second type of infinite chains. This hypothetical polymorph has not been found in silicates, however it is essentially the structure of the $Zn_{11}\square(HPO_3)_8(OH)_6$ and tellurate phases (but the tellurate–dumortierite relation was not established in (*16*) nor in (*22*)).

We also could relate these structures with those of more distant materials in which ordering of $[MO_6]$ octahedra around a pinwheel is more or less similar but with simple pyroxene-like chains instead of double chains. Examples may be $Li_3Fe(MoO_4)_3$, $Li_2Fe_2(MoO_4)_3$ (*24*), $NaCo_{2.31}(MoO_4)_3$ (*25*), and Lyonsite $Cu_3Fe_4(VO_4)_6$ (*26*). By simple displacement of some oxygen atoms, the $[MO_6]$ octahedron is sometimes partly replaced by trigonal prism occupied either by Li or Na atoms: this was the reason that we have considered the possibility of a sodium presence in our compound at the structure determination stage.

All the materials mentioned above illustrate the extraordinary versatility of such a structure type. We are currently interested in the possible isomorphic substitution of the Zn atom for Co or Ni atoms, because interesting magnetic properties are expected. Moreover, it may be emphasized that isotypic phases could be imagined built up from other tetrahedral species than the

pseudo-HPO_3 ones, giving rise to a different crystal chemistry inside the channels. Work is in progress.

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