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Refinement of the Structure of Synthetic Sodium Zinc Monophosphate

J. YAMAKAWA, I. WATANABE AND A. KAWAHARA

Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima-Naka 3-1-1, Okayama 700, Japan

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Abstract

The title structure, $Zn_2NaH(PO_4)_2$, belongs to the monophosphate group and contains two kinds of PO_4 tetrahedra connected by two kinds of ZnO_4 distorted tetrahedra. These four kinds of tetrahedra are connected by corner sharing to form sheets parallel to the *ac* plane. The PO_4 tetrahedra are isolated from each other in the sheets. The Na and H atoms are located between the sheets. The Na atoms have six O atoms as nearest neighbours. The H atoms are connected to the apex O atoms of two adjacent sheets by hydrogen bonding.

Comment

A series of Fe–Zn–Na phosphates have been synthesized (Kabalov, Yakubovich, Simonov & Belov, 1975) and the structure of one, the title compound, has been determined by Kabalov, Simonov, Yakubovich & Belov (1974). However, in their study the standard deviations of the geometric parameters were not estimated and the positions of the H atoms were not determined. On consideration of spectroscopic and other physical studies based on the crystal structure data, it was deemed necessary to perform a more accurate refinement of the geometric parameters of this compound, and so in this study, the atomic parameters were further refined and the H-atom positions determined.

The chemical composition was confirmed as $Zn_2NaH(PO_4)_2$ on the basis of molecular ratios of Na, P and Zn atoms, determined by electron microprobe analyses. A stereoview (*ORTEP*II; Johnson, 1971) of the compound is presented in Fig. 1. The positions of the H atoms were determined from difference syntheses and confirmed by the calculation of the sum of electrostatic charges around connected O atoms (Brown & Wu, 1976). The configuration around the hydrogen bond is illustrated in Fig. 2. The distance O(1)···O(2) 2.69 (1) Å corresponds to a hydrogen bond.

The interatomic distances and angles are compatible with those of related compounds, *e.g.* $NaZnPO_4$ (Elammar, Durand, Cot & Elouadi, 1987), and those found in a general review of the structure of phosphates (Corbridge, 1971).

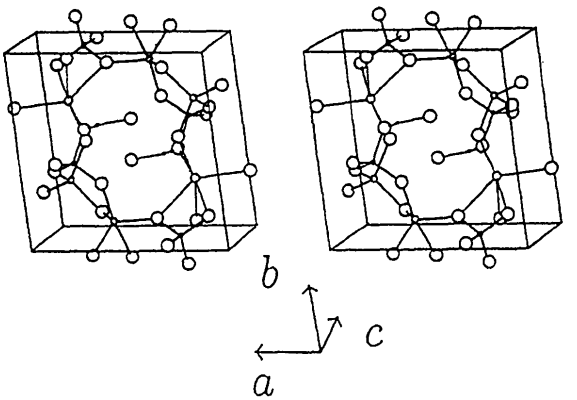

Fig. 1. Stereoview of $Zn_2NaH(PO_4)_2$. The filled small circles represent P and the large open circles O atoms. Small and medium open circles correspond to Zn and N atoms, respectively.

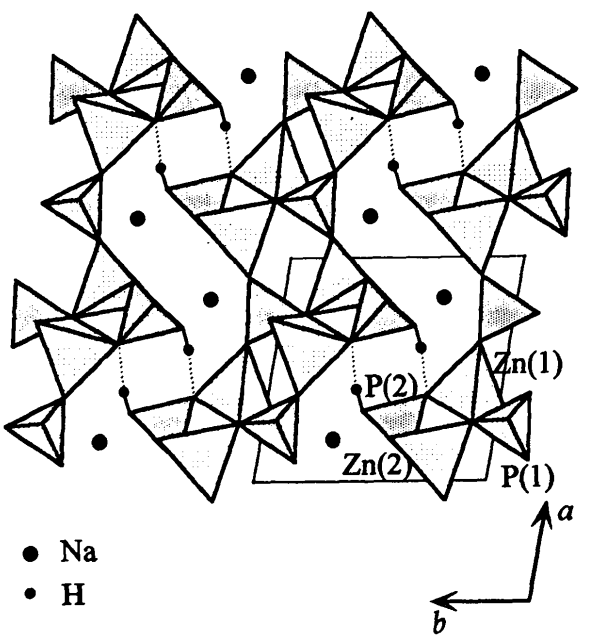

Fig. 2. The linkage of coordination polyhedra of Zn and P atoms. Two tetrahedra of ZnO_4 are connected by corner sharing. PO_4 tetrahedra are inserted among these Zn_2O_7 tetrahedra to form zigzag sheets parallel to the *ac* plane.

Experimental

The title compound was obtained after heating a reagent mixture of $Zn_2(PO_4)_3.4H_2O$ and $Na_2SO_4.2H_2O$ at 773 K and

200 kg cm^{-2} pressure. This was then sealed in silver tubes with a CH_3COOH solution (pH 4). The ends of tubes were sealed by welding. The tubes were placed in Tuttle-type apparatus and heated for 3 d in an electric furnace. They were then cooled at a rate of 1° per 20 mins. The crystals obtained were washed with pure water after cooling.

Crystal data

$Zn_2NaH(PO_4)_2$
M_r = 344.70
Triclinic
$P\bar{1}$
a = 8.621 (2) Å
b = 8.799 (2) Å
c = 5.115 (1) Å
α = 100.44 (2)°
β = 105.79 (2)°
γ = 96.94 (2)°
V = 361.1 (1) $Å^3$
Z = 2
D_x = 3.17 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 20-27.5°
μ = 7.314 mm^{-1}
T = 297 K
Prismatic
0.06 × 0.04 × 0.04 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω-scans
Absorption correction: none
1799 measured reflections
1799 independent reflections
1394 observed reflections [$F > 3\sigma(F)$]
θ_{max} = 27.5°
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -7 \rightarrow 7$
3 standard reflections monitored every 300 reflections
intensity variation: 0.3%

Refinement

Refinement on F
R = 0.043
wR = 0.048
S = 1.04
1394 reflections
137 parameters
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.12
$\Delta\rho_{max}$ = 1.21 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.01 e $Å^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Zn(1)	0.3827 (1)	0.1070 (1)	0.6696 (2)	0.86 (2)
Zn(2)	0.1119 (1)	0.2594 (1)	0.2211 (2)	0.86 (1)
Na	0.1863 (4)	0.6882 (3)	0.4090 (6)	1.33 (7)
P(1)	0.2442 (2)	0.4181 (2)	0.8389 (4)	0.78 (4)
P(2)	0.2504 (2)	0.9398 (2)	0.0922 (4)	0.80 (4)
O(1)	0.3792 (7)	0.3198 (6)	0.8623 (11)	1.37 (14)
O(2)	0.3142 (7)	0.5835 (6)	0.7949 (11)	1.40 (13)
O(3)	0.1957 (7)	0.4447 (6)	0.1053 (10)	1.30 (14)
O(4)	0.2592 (7)	0.1059 (6)	0.2721 (10)	1.08 (13)
O(5)	0.0952 (6)	0.3481 (6)	0.5859 (10)	1.04 (13)
O(6)	0.0884 (7)	0.8355 (6)	0.0556 (11)	1.47 (13)
O(7)	0.3844 (6)	0.8722 (6)	0.2750 (11)	1.28 (13)
O(8)	0.2748 (7)	0.9508 (6)	0.8107 (10)	1.51 (14)
H	0.59 (2)	0.38 (1)	0.08 (2)	

Table 2. *Selected geometric parameters* (Å, °)

Zn(1)—O(1)	1.959 (5)	Na—O(7)	2.526 (7)
Zn(1)—O(4)	2.020 (5)	Na—O(8)	2.673 (5)
Zn(1)—O(7^{i})	1.931 (5)	P(1)—O(1)	1.524 (6)
Zn(1)—O(8^{ii})	1.921 (5)	P(1)—O(2)	1.585 (6)
Zn(2)—O(3)	1.957 (6)	P(1)—O(3^{v})	1.518 (6)
Zn(2)—O(4)	1.966 (6)	P(1)—O(5)	1.523 (4)
Zn(2)—O(5)	1.938 (5)	P(2)—O(4^{vi})	1.561 (5)
Zn(2)—O(6^{iii})	1.891 (5)	P(2)—O(6)	1.521 (6)
Na—O(2)	2.383 (6)	P(2)—O(7)	1.530 (6)
Na—O(3)	2.432 (6)	P(2)—O(8^{vii})	1.529 (6)
Na—O(5^{iv})	2.417 (6)	H—O(1^{vi})	1.81 (11)
Na—O(6)	2.438 (7)	H—O(2^{ii})	0.87 (10)
O(1)—Zn(1)—O(4)	101.5 (2)	O(1)—P(1)—O(3^{v})	110.6 (3)
O(1)—Zn(1)—O(7^{i})	98.5 (2)	O(1)—P(1)—O(5)	112.9 (3)
O(1)—Zn(1)—O(8^{ii})	111.4 (3)	O(2)—P(1)—O(3^{v})	108.4 (3)
O(4)—Zn(1)—O(7^{ii})	111.5 (3)	O(2)—P(1)—O(5)	105.9 (3)
O(4)—Zn(1)—O(8^{ii})	111.9 (2)	O(3^{v})—P(1)—O(5)	111.0 (3)
O(7^{ii})—Zn(1)—O(8^{i})	119.7 (3)	O(4^{vi})—P(2)—O(6)	109.9 (3)
O(3)—Zn(2)—O(4)	115.2 (3)	O(4^{vi})—P(2)—O(7)	104.0 (3)
O(3)—Zn(2)—O(5)	102.7 (2)	O(4^{vii})—P(2)—O(8^{vi})	111.2 (3)
O(3)—Zn(2)—O(6^{iii})	106.1 (2)	O(6)—P(2)—O(7)	106.6 (3)
O(4)—Zn(2)—O(5)	106.9 (2)	O(6)—P(2)—O(8^{vii})	111.3 (3)
O(4)—Zn(2)—O(6^{iii})	110.2 (2)	O(7)—P(2)—O(8^{vii})	113.5 (3)
O(5)—Zn(2)—O(6^{iii})	115.7 (2)	O(1^{vi})—H—O(2^{ii})	169 (12)
O(1)—P(1)—O(2)	107.8 (3)		

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, 1-y, -z$; (iv) $-x, 1-y, 1-z$; (v) $x, y, 1+z$; (vi) $x, y, z-1$; (vii) $x, 1+y, z$.

Refinement was by full-matrix least squares. The positions of the H atoms were determined from difference syntheses and confirmed by the calculation of the sum of electrostatic charges around connected O atoms (Brown & Wu, 1976). Data collection, cell refinement and data reduction: *AFC/MSC Diffractometer Control Software* (Rigaku Corporation, 1991). Program(s) used to refine structure: *RSFLS-4 UNICS* (Sakurai, 1971). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *LISTHKL* (Yamakawa & Kawahara, 1992).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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