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A Cubic Hydrated Sodium Zinc Phosphate with a Tetrahedral-Triangular Framework Topology, $Na_6Zn_3(PO_4)_4.3H_2O$

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Abstract

The structure of hexasodium trizinc tetraphosphate trihydrate has been refined from a twinned crystal. The three-dimensional framework consists of strictly alternating Zn and P oxygen tetrahedra with Na cations and water molecules located inside the cages.

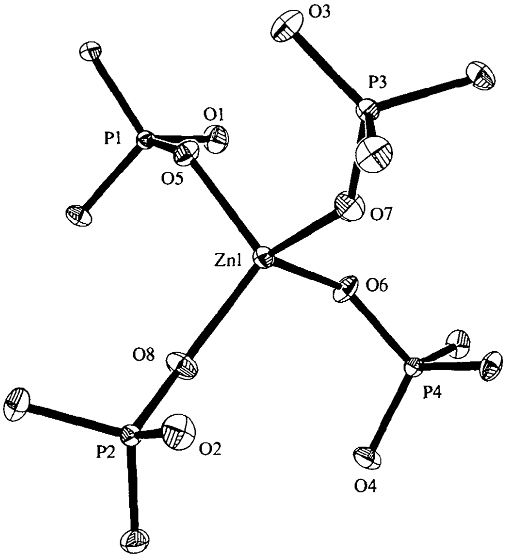

Fig. 1. View of the Zn and P tetrahedra with 50% probability displacement ellipsoids and atomic labelling. Two unique Na^+ cations and one unique water molecule are omitted.

Comment

Interest in non-aluminosilicate molecular sieves has resulted in a large number of phosphate-based novel framework materials. Examples include alumino-(or gallo)phosphates (Flanigen, 1991), zinco(or beryllo)-phosphates (Gier & Stucky, 1991; Feng, Bu & Stucky, 1995; Bu, Feng & Stucky, 1996), and cobalt phosphates (Feng, Bu & Stucky, 1997*a*; Feng, Bu, Tolbert & Stucky, 1997). Our own studies have led to several dozen new open-framework metal phosphates and arsenates including about three dozen new materials with topology isotypic with known zeolite structures (Feng, Bu & Stucky, 1997*b*; Bu, Feng, Gier & Stucky, 1997).

We have previously reported the synthesis and preliminary characterizations of a cubic sodium zinc phosphate, $Na_6Zn_3(PO_4)_4.3H_2O$ (Gier, Harrison, Nenoff & Stucky, 1992). The structure analysis was, however, not satisfactory due to the crystal twinning and the associated pseudosymmetry. We have now resolved the twinning problem and the new structure refinement allows accurate determination of the cubic structure including the location and refinement of water-molecule H-atom positions. In this paper, we report the structural analysis of $Na_6Zn_3(PO_4)_4.3H_2O$.

There is one unique Zn-atom site and four P-atom sites. One important structural feature is that there is a pendant P=O group on each PO_4^{3-} group (O1, O2, O3 and O4 are pendant O atoms on P1, P2, P3 and P4, respectively). The remaining framework O atoms (O5, O6, O7 and O8) are bicoordinated to one Zn atom and one P atom (excluding coordination to extra-framework Na atoms). Thus, in terms of the framework connectivity, all P atoms are tricoordinate. There are no four- or six-membered rings (*i.e.* four or six polyhedral atoms such as P and Zn in a ring excluding O-atom bridges). The framework consists of highly distorted eight-membered rings.

Compared to zeolite frameworks which consist of alternating tetrahedral centers, the framework of the title compound consists of four-connected Zn-atom tetrahedra in strict alternation with three-connected P-atom tetrahedra. This explains the ratio of 3/4 for Zn/P. Another framework structure that consists of four- and three-connected polyhedral centers is $Na_2Zn_3(CO_3)_4.3H_2O$ (Gier, Bu, Wang & Stucky, 1996). The title compound is isostructural with $Na_6As_3(PO_4)_4.3H_2O$ (Grey, Madsen, Jones & Smith, 1989).

Each of the two unique sodium cations (Na1 and Na2) is located in a slightly distorted octahedral environment. One of the six O atoms (O9) in the sodium coordination sphere belongs to a water molecule. Both H atoms on the water molecule are hydrogen bonded to the framework O atoms. The bonding distances H91···O5 and H92···O6 are 1.99 (5) and 2.06 (7) Å, respectively.

The crystal used for data collection is a reflection twin. The twin plane is parallel to the *c* axis and bisects the *a* and *b* axes. The volume ratio between the two twin domains is 79:21 [the refined value is 0.2113 (3)].

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Experimental

The title compound was prepared by hydrothermal synthesis (Gier, Harrison, Nenoff & Stucky, 1992).

Crystal data

$Na_6Zn_3(PO_4)_4.3H_2O$
$M_r = 767.98$
Cubic
$P2_13$
$a = 11.99310\,(10)$ Å
$V = 1725.02\,(2)$ Å^3
$Z = 4$
$D_x = 2.957$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.70$–$28.28°$
$\mu = 4.762$ mm^{-1}
$T = 293\,(2)$ K
Translucent cube
$0.12 \times 0.12 \times 0.12$ mm
Colorless

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical from diffraction data (Blessing, 1995; Sheldrick, 1996)
$T_{min} = 0.61$, $T_{max} = 0.67$

17 981 measured reflections
1434 independent reflections
1411 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 28.18°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.047$
$S = 1.016$
1434 reflections
107 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0180P)^2 + 3.0057P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.008$

$\Delta\rho_{max} = 0.278$ e Å^{-3}
$\Delta\rho_{min} = -0.248$ e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1995*b*)
Extinction coefficient: 0.00029 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983) parameter = 0.006 (11)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Zn1	0.37493 (4)	0.00257 (4)	0.24292 (3)	0.01019 (9)
P1	0.51982 (7)	$1/2-x$	$-1/2+x$	0.0085 (3)
P2	0.52961 (7)	$-1/2+x$	$1-x$	0.0089 (3)
P3	0.21866 (7)	$-x$	$1/2-x$	0.0090 (3)
P4	0.22983 (7)	x	x	0.0087 (3)
O1	0.4476 (2)	$1/2-x$	$-1/2+x$	0.0174 (9)
O2	0.4574 (2)	$-1/2+x$	$1-x$	0.0175 (9)
O3	0.2913 (2)	$-x$	$1/2-x$	0.0201 (10)
O4	0.3025 (2)	x	x	0.0166 (9)
O5	0.4544 (2)	−0.0691 (2)	0.1202 (2)	0.0126 (5)
O6	0.2974 (2)	0.1334 (2)	0.1758 (2)	0.0142 (5)
O7	0.2587 (2)	−0.0959 (2)	0.2888 (2)	0.0164 (5)
O8	0.4805 (2)	0.0514 (2)	0.3526 (2)	0.0159 (5)
Na1	0.33262 (15)	0.50225 (13)	0.24862 (11)	0.0228 (4)
Na2	0.42141 (14)	0.00771 (12)	0.74104 (12)	0.0207 (3)
O9	0.5010 (3)	0.2468 (2)	0.1283 (3)	0.0249 (5)

Table 2. *Selected geometric parameters (Å)*

Zn1—O7	1.908 (2)	P4—O4	1.509 (5)
Zn1—O8	1.917 (2)	P4—O6^{vii}	1.554 (2)
Zn1—O5	1.953 (2)	P4—O6	1.554 (2)
Zn1—O6	1.994 (2)	P4—O6^{viii}	1.554 (2)
P1—O1	1.500 (5)	O4—Na1^{vii}	2.508 (3)
P1—O5	1.554 (2)	Na1—O5^{ix}	2.317 (3)
P1—O5^{i}	1.554 (2)	Na1—O8^{vii}	2.392 (3)
P1—O5^{ii}	1.554 (2)	Na1—O9^{vii}	2.450 (4)
P2—O2	1.500 (5)	Na1—O3^{x}	2.570 (3)
P2—O8^{iii}	1.553 (2)	Na1—O8^{xi}	2.616 (3)
P2—O8	1.553 (2)	Na2—O6^{xii}	2.394 (3)
P2—O8^{iv}	1.553 (2)	Na2—O7^{iv}	2.449 (3)
P3—O3	1.510 (5)	Na2—O7^{xiii}	2.472 (3)
P3—O7^{v}	1.551 (2)	Na2—O9^{xiv}	2.488 (4)
P3—O7^{vi}	1.551 (2)	Na2—O1^{xv}	2.554 (3)
P3—O7	1.551 (2)	Na2—O2	2.493 (3)

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

The data collection nominally covered over a full sphere of reciprocal space by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm. The total number of exposures is 2082. The coverage of the data set is 100% at every resolution to at least 28° in θ.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1995*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1187). Services for accessing these data are described at the back of the journal.

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$Cs_5Mo_{21}S_{23}$

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Abstract

Pentacaesium henicosamolybdenum tricosasulfur is isostructural with $Cs_5Mo_{21}Se_{23}$ and is the third member in the series $M_{2n-1}Mo_{6n+3}X_{6n+5}$ (M = Rb, Cs; X = S, Se, Te). Its crystal structure contains as the main building block an $Mo_{21}S_{23}$ cluster unit, the Mo core of which consists of six face-sharing Mo_6 octahedra. The decrease in the ionic radius of the chalcogen results in a shortening of the Mo—Mo intertriangle distances while the intratriangle ones do not change significantly. The shortest intercluster Mo—Mo distance also decreases from 3.342 (3) Å in $Cs_5Mo_{21}Se_{23}$ to 3.1687 (9) Å in $Cs_5Mo_{21}S_{23}$.

Comment

This work is part of our programme in search of new reduced molybdenum compounds in the Cs–Mo–S system. Until now, this study has led to the synthesis of six structure types by solid-state reaction: $Cs_{0.6}Mo_6S_7$ (Gougeon, Padiou, Potel, Sergent & Couach, 1984), which contains Mo_6 clusters; $Cs_6Mo_{24}S_{26}$ and $Cs_8Mo_{30}S_{32}$ (Gougeon, 1984), comprising condensed clusters built up from seven or nine Mo_6 clusters; and infinite chains of *trans*-face-shared Mo_6 octahedra in the quasi-one-dimensional compound $Cs_2Mo_6S_6$ (Potel, 1981). In addition, mixtures of Mo_6 and Mo_9 clusters ($Cs_2Mo_{15}S_{19}$; Gougeon, 1988), and Mo_9 and Mo_{12} clusters ($Cs_4Mo_{21}S_{25}$; Gougeon & Potel, 1993) have also been obtained. Here we present the crystal structure of a new compound belonging to the Cs–Mo–S system, $Cs_5Mo_{21}S_{23}$.

A view of the structure of $Cs_5Mo_{21}S_{23}$ is shown in Fig. 1. The basic structural unit is the $Mo_{21}S_{23}$ cluster unit (Fig. 2) which can be thought of as six Mo_6S_8 units fused together sharing Mo_3S_3 faces, after removal of the capping S atoms. Consequently, the Mo atoms belonging to the outer Mo_3 triangles have an environment similar to that of the Mo atoms of the Mo_6S_8 cluster units (five S and four Mo), while those of the inner triangles are surrounded by six Mo atoms and four S atoms. In addition, all the S atoms which are coplanar with the shared octahedral faces bridge two triangular faces and the others bridge one triangular face.

As observed previously in $Cs_5Mo_{21}Se_{23}$ (Gougeon, Potel & Sergent, 1990) and compounds of the series $M_{2n-2}Mo_{6n}X_{6n+2}$ containing $Mo_{6n}X_{6n+2}$ cluster units (n = 2, 3, 4 and 5) (Gougeon, 1984), the distances between Mo atoms related through the threefold axis (intratriangle distances) lie in a narrow range [2.6587 (11)–2.6688 (8) Å] whereas those between adjacent Mo_3 triangles (intertriangle distances) vary from 2.6699 (6) to 2.7539 (7) Å. The intratriangle Mo—Mo distances are somewhat similar to those in $Cs_5Mo_{21}Se_{23}$ [2.652 (2)–2.669 (2) Å], and the intertriangle distances are smaller than comparable values in $Cs_5Mo_{21}Se_{23}$ [2.701 (2)–2.768 (2) Å], as expected from the smaller radius of the S atom. This contraction of the Mo_{21} cluster along its elongation axis is reflected in the spacings between Mo_3 triangles which are 2.275 Å for $\Delta(1)$–$\Delta(2)$, 2.194 Å for $\Delta(2)$–$\Delta(3)$ and 2.206 Å for $\Delta(3)$–$\Delta(4)$ in $Cs_5Mo_{21}S_{23}$

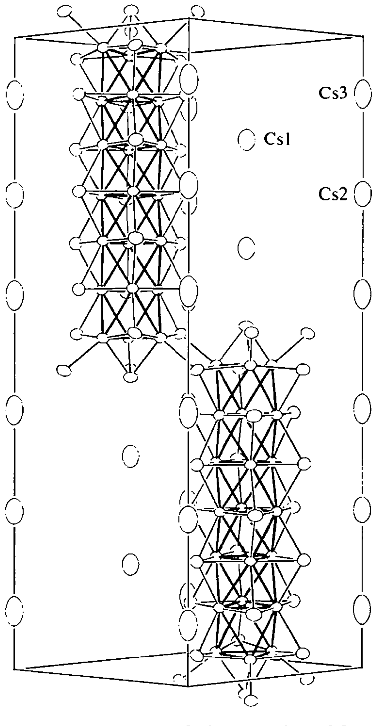

Fig. 1. View of the unit cell of $Cs_5Mo_{21}S_{23}$. Mo_{21} clusters are emphasised by thick lines. Mo—S bonds are shown as thin lines. Unconnected ellipsoids represent the Cs^+ cations. Displacement ellipsoids are drawn at the 95% probability level.

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