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The high-temperature modification of zinc *catena*-polyphosphate, β-Zn(PO$_3$)$_2$

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Single crystals of the high-temperature modification of zinc *catena*-polyphosphate, β-Zn(PO$_3$)$_2$, were grown from a melt and quenched from 1093 K to room temperature. The structure was solved from single-crystal X-ray diffraction data and is built of corrugated $(PO_3)_\infty$ polyphosphate chains, which extend along the *c* direction with an eight-tetrahedra repeat. Slightly distorted [ZnO$_4$] tetrahedra link the polyphosphate chains into a three-dimensional network.

Comment

Interest in materials with open-framework architectures has increased enormously in the past few years; in particular, solids based on organically templated phosphate networks have been investigated thoroughly (Cheetham *et al.*, 1999). Among the open-framework materials, zinc phosphates have an exceptional position because their structural variety results in different physicochemical properties (Neeraj & Natarajan, 2001). Additionally, some of these zinc phosphates form analogous aluminosilicate zeolite structures as a result of the formation of [ZnO$_4$] tetrahedral units, which makes these materials very promising for application on a large industrial scale. Frequently, these materials have to be treated thermally to expel the template molecules, and at higher temperatures, thermolysis results in the formation of inorganic zinc phosphates, which also exhibit a diverse and interesting crystal chemistry.

Phase equilibria in the ZnO–P$_2$O$_5$ system were investigated for the first time by Katnack & Hummel (1958), who showed that three congruently melting phases exist, *viz*. Zn$_3$(PO$_4$)$_2$, Zn$_2$P$_2$O$_7$ and Zn(PO$_3$)$_2$, all of which are polymorphic. Two polymorphic forms of zinc ultraphosphate with a Zn/P ratio of 1:4 have also been reported in the ZnO–P$_2$O$_5$ system. Since ultraphosphates are difficult to prepare by conventional ceramic methods, no phases with this composition were observed during Katnack & Hummel's investigation. Up to now, the following anhydrous zinc phosphate structures have been reported [the coordination numbers (CN) of the unique Zn atoms are given in parentheses]: three zinc orthophosphates, α-Zn$_3$(PO$_4$)$_2$ (2×4; Calvo, 1965*a*), β-Zn$_3$(PO$_4$)$_2$ (2×5, 1×6; Stephens & Calvo, 1967) and γ-Zn$_3$(PO$_4$)$_2$ (1×5, 1×6; Calvo, 1963); three diphosphates, α-Zn$_2$P$_2$O$_7$ (2×5, 1×6; Robertson & Calvo, 1970), β-Zn$_2$P$_2$O$_7$ (1×6; Calvo, 1965*b*) and γ-Zn$_2$P$_2$O$_7$ (2×5; Bataille *et al.*, 1998); two modifications of the ultraphosphate ZnP$_4$O$_{11}$, one with a 16–4-membered (1×6; Baez-Doelle *et al.*, 1993) and one with a 10–10-membered phosphate framework (2×6; Weil & Glaum, 1998); and phosphates with a Zn/P ratio of 1:2. For the latter, three different phases are reported, *viz*. a *cyclo*-tetrametaphosphate, Zn$_2$P$_4$O$_{12}$, which is isotypic with the corresponding M_2P$_4$O$_{12}$ structures [M = Ni, Mg, Cu, Co, Mn and Fe; CN(M) = 6; Beucher & Grenier, 1968; Bagieu-Beucher *et al.*, 1976], and two long-chain polyphosphates, Zn(PO$_3$)$_2$, *viz*. one of the low-temperature α form [CN(Zn) = 6; Averbuch-Pouchot *et al.*, 1983] and one of the high-temperature β form. Although the thermal transformations of these Zn tetrameta- and polyphosphates have been the subject of several investigations (Thilo & Grunze, 1957; Nirsha *et al.*, 1982; Trojan, 1990; Takenaka & Matsuda, 2002), no structural details for β-Zn(PO$_3$)$_2$ have been reported previously. For this latter phase, only lattice parameters have been reported (Schultz, 1974), and therefore, single-crystal growth experiments for subsequent structure determination were begun.

The high-temperature polymorph β-Zn(PO$_3$)$_2$ crystallizes in a new structure type and shows no close relationship with the low-temperature α polymorph. In the α polymorph, chains of distorted edge-sharing [ZnO$_6$] octahedra extend along the *c* direction, and the $(PO_3)_\infty$ chains run parallel to the cationic chains, with a period of two PO$_4$ tetrahedra. This compact arrangement results in a very regular layered organization, and the density of α-Zn(PO$_3$)$_2$ (3.641 Mg m^{-3}; volume 16.97 Å^3 per O atom) is much higher than that of β-Zn(PO$_3$)$_2$ (3.129 Mg m^{-3} and 19.75 Å^3 per O atom). The high-temperature polymorph contains two Zn, four P and 12 O atoms in the asymmetric unit. The Zn atoms are tetrahedrally coordinated, and each [ZnO$_4$] tetrahedron shares its four corners with four adjacent PO$_4$ tetrahedra, resulting in a layered assembly parallel to the $(1\bar{1}0)$ plane (Fig. 1). The $(PO_3)_\infty$ polyphosphate chains cross the unit cell parallel to the *c* direction, with a period of eight PO$_4$ tetrahedra (P4, P1, P2, P3, P4′, P1′, P2′ and P3′; Fig. 2). The distorted PO$_4$ tetrahedra display the bond-length distribution observed for various polyphosphate structures (Durif, 1995), with two significantly longer bridging P—O bonds [mean 1.586 (7) Å] and two shorter terminal P—O bonds [mean 1.474 (8) Å]. The mean P—O—P angle [135 (3)°] is also in the characteristic range for long-chain polyphosphates. Both [ZnO$_4$] tetrahedra are considerably distorted, with Zn—O distances in the range 1.9044 (19)–1.9553 (18) Å [mean 1.93 (2) Å], which is in good agreement with the values found for other structures that contain tetrahedral [ZnO$_4$] units. The coordination number of all O atoms is two. Except for the bridging O3, O5, O11 and O12 atoms of the polyphosphate chain, all O atoms are bonded to one Zn and one P atom.

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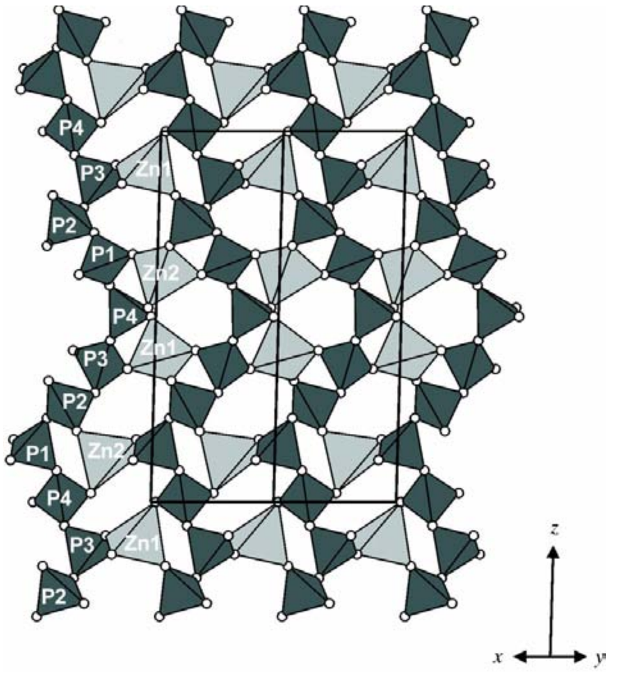

Figure 1
A projection of the β-$Zn(PO_3)_2$ crystal structure along [110]. The polyphosphate chains are shown in dark grey and the $[ZnO_4]$ tetrahedra are shown in light grey.

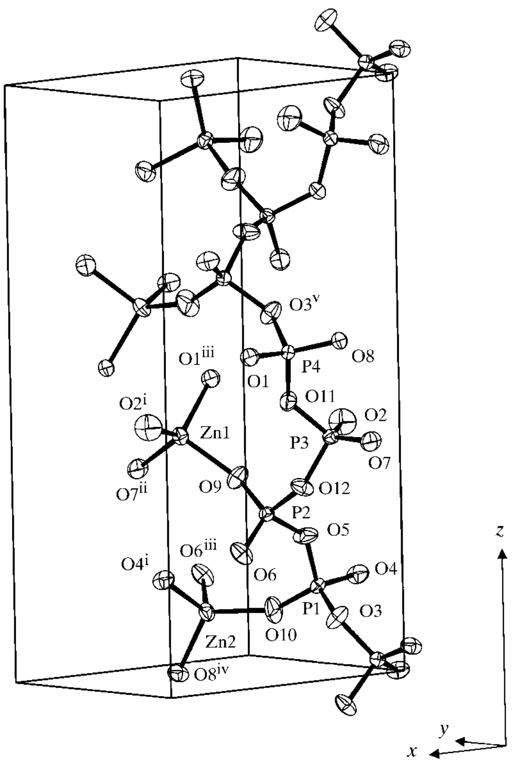

Figure 2
A plot of the corrugated polyphosphate chain with attached $[ZnO_4]$ tetrahedra. The anisotropic displacement ellipsoids are drawn at the 74% probability level. Symmetry codes are given in Table 1.

Results of bond-valence calculations, using the parameters of Brese & O'Keeffe (1991), are in accordance with expected values and reflect the small distortions in the $[ZnO_4]$ and PO_4 tetrahedra (Zn1 2.19, Zn2 2.18, P1 4.98, P2 4.95, P3 4.96, P4 4.88, O1 1.88, O2 2.03, O3 2.08, O4 1.99, O5 2.15, O6 1.93, O7 2.03, O8 1.91, O9 1.95, O10 2.03, O11 2.08 and O12 2.10).

Experimental

For the preparation of pure zinc polyphosphate, a slight excess of the phosphate source (~2%) is recommended (Thilo & Grunze, 1957). In a typical experiment, ZnO (0.364 g, Aldrich, p.A.) and $(NH_4)_2HPO_4$ (1.204 g, Merck, p.A.) were mixed thoroughly and milled in an agate mortar. The powder was then placed in a platinum crucible and put in a conventional laboratory furnace, which was programmed as follows: room temperature → 1163 K (3 h) → 1093 K (17 h). The platinum crucible was then removed from the furnace and immediately quenched to room temperature using a cold-water bath. The resulting solidified melt was crushed and examined under a polarizing microscope. Colourless crystals of the title compound, of an unspecific habit and up to 0.3 mm in length, were isolated. Powder X-ray diffraction of the bulk material revealed β-$Zn(PO_3)_2$ as a single-phase product. The powder data are consistent with those reported by Katnack & Hummel (1958) and the lattice parameters are in very good agreement with those reported by Schultz (1974).

Crystal data

$Zn(PO_3)_2$
$M_r = 223.31$
Monoclinic, *Cc*
$a = 7.6353$ (8) Å
$b = 7.6077$ (8) Å
$c = 16.335$ (2) Å
$\beta = 92.190$ (9)°
$V = 948.17$ (19) Å^3
$Z = 8$

$D_x = 3.129$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.0$–16.6°
$\mu = 5.80$ mm^{-1}
$T = 293$ (2) K
Fragment, colourless
0.20 × 0.16 × 0.14 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993–1997)
$T_{min} = 0.454$, $T_{max} = 0.538$
6620 measured reflections
3424 independent reflections

3242 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 32.5°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -24 \rightarrow 24$
3 standard reflections frequency: 300 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.043$
$S = 1.03$
3424 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00160 (13)
Absolute structure: Flack & Bernardinelli (1999), 1714 Friedel pairs
Flack parameter = −0.001 (6)

Systematic absences revealed the possible space groups *Cc* and *C*2/*c*. For the latter, no reasonable structure solution was obtained using either direct methods or a Patterson synthesis with *SHELXS*97 (Sheldrick, 1990). For the structure determination in the *Cc* space group, the Zn- and P-atom positions were obtained from direct

Table 1
Selected geometric parameters (Å, °).

Zn1—O2^{i}	1.9044 (19)	P2—O9	1.4725 (18)
Zn1—O7^{ii}	1.9110 (18)	P2—O6	1.4745 (18)
Zn1—O9	1.9418 (18)	P2—O5	1.5807 (19)
Zn1—O1^{iii}	1.9541 (17)	P2—O12	1.5906 (18)
Zn2—O4^{i}	1.9088 (17)	P3—O7	1.4648 (18)
Zn2—O10	1.9120 (18)	P3—O2	1.468 (2)
Zn2—O8^{iv}	1.9433 (16)	P3—O12	1.5829 (17)
Zn2—O6^{iii}	1.9553 (18)	P3—O11	1.5946 (17)
P1—O10	1.4648 (18)	P4—O8	1.4834 (17)
P1—O4	1.4743 (18)	P4—O1	1.4872 (17)
P1—O5	1.5741 (18)	P4—O11	1.5827 (17)
P1—O3	1.5954 (18)	P4—O3^{v}	1.5842 (17)

O2^{i}—Zn1—O7^{ii}	110.24 (10)	O6—P2—O5	110.87 (10)
O2^{i}—Zn1—O9	108.86 (10)	O9—P2—O12	110.08 (11)
O7^{ii}—Zn1—O9	107.12 (8)	O6—P2—O12	107.18 (10)
O2^{i}—Zn1—O1^{iii}	118.23 (8)	O5—P2—O12	100.46 (11)
O7^{ii}—Zn1—O1^{iii}	110.96 (8)	O7—P3—O2	118.76 (13)
O9—Zn1—O1^{iii}	100.47 (8)	O7—P3—O12	105.99 (11)
O4^{i}—Zn2—O10	111.74 (9)	O2—P3—O12	111.54 (11)
O4^{i}—Zn2—O8^{iv}	110.45 (8)	O7—P3—O11	111.88 (10)
O10—Zn2—O8^{iv}	120.28 (8)	O2—P3—O11	107.47 (12)
O4^{i}—Zn2—O6^{iii}	106.45 (8)	O12—P3—O11	99.55 (10)
O10—Zn2—O6^{iii}	107.57 (9)	O8—P4—O1	119.53 (11)
O8^{iv}—Zn2—O6^{iii}	98.65 (7)	O8—P4—O11	108.47 (10)
O10—P1—O4	118.38 (13)	O1—P4—O11	107.93 (10)
O10—P1—O5	112.43 (12)	O8—P4—O3^{v}	108.17 (10)
O4—P1—O5	105.29 (10)	O1—P4—O3^{v}	109.06 (10)
O10—P1—O3	107.68 (12)	O11—P4—O3^{v}	102.33 (10)
O4—P1—O3	110.94 (10)	P4^{vi}—O3—P1	133.22 (12)
O5—P1—O3	100.74 (10)	P1—O5—P2	139.21 (13)
O9—P2—O6	119.83 (12)	P4—O11—P3	133.80 (11)
O9—P2—O5	106.72 (12)	P3—O12—P2	133.32 (12)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $1+x, y, z$; (iii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iv) $1+x, 1-y, z-\frac{1}{2}$; (v) $x, 1-y, \frac{1}{2}+z$; (vi) $x, 1-y, z-\frac{1}{2}$.

methods and the O-atom positions were obtained from subsequent Fourier syntheses. Analysis of the refined atomic coordinates with *PLATON* (Spek, 2003) showed no higher symmetry. Moreover, the Flack parameter (Flack & Bernardinelli, 1999) gives a clear indication of the absence of a centre of symmetry.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* in *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1027). Services for accessing these data are described at the back of the journal.

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