

[Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}]Jovica Stojanović,^{a*} Tamara Đordjević^b and Ljiljana Karanović^c

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The structure of the title compound, ammineaquadi- μ_5 -phosphato-trizinc(II), [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}], consists of two parts: (i) PO₄ and ZnO₄ vertex-sharing tetrahedra arranged in layers parallel to (100) and (ii) ZnO₂(N/O)₂ tetrahedra located between the layers. Elemental analysis establishes the ammine-to-water ratio as 3:2. ZnO₂(N/O)₂ tetrahedra are located at special position 4*e* (site symmetry 2) in *C2/c*. The two O atoms of ZnO₂(N/O)₂ are bonded to neighbouring P atoms, forming two Zn—O—P linkages and connecting ZnO₂(N/O)₂ tetrahedra with two adjacent *bc* plane layers. A noteworthy feature of the structure is the presence of NH₃ and H₂O at the same crystallographic position and, consequently, qualitative changes in the pattern of hydrogen bonding and weaker N/O—H...O electrostatic interactions, as compared to two closely related structures.

Comment

This work forms part of ongoing research on heteropolyhedral framework structures of divalent metal phosphates and arsenates with potentially interesting structural, physical and chemical properties (Đordjević *et al.*, 2008; Đordjević & Karanović, 2008; Stojanović *et al.*, 2008; Weil *et al.*, 2009). The aim of the current study was the synthesis and characterization of new compounds in the CdO—ZnO—P₂O₅—NH₃—H₂O system. Using the low-temperature hydrothermal method, single crystals of ammineaquadi- μ_5 -phosphato-trizinc(II), [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}], were synthesized.

The crystal structure of [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}] is constructed from corrugate layers parallel to the *bc* plane, containing slightly distorted vertex-sharing P1O₄ and Zn2O₄ tetrahedra. The space between these layers is bounded by $x \approx 0.39$ and $x \approx 0.61$ (Fig. 1).

Considering the network of Zn2—O and P1—O bonds, the layers can be described as being composed of six- and eight-membered rings formed by congeners of Zn2, O and P1, in

which O can be O2, O3 or O4 (Figs. 2 and 3). Each eight-membered —Zn2/O/P1— ring is formed by alternating corner-sharing pairs of Zn2O₄ and P1O₄ tetrahedra, while one P1O₄ and two symmetry-related Zn2O₄ tetrahedra are connected at shared corners to form each six-membered Zn2—O2—P1—O4—Zn2^v—O4ⁱⁱⁱ ring (symmetry codes from Fig. 3). The eight-membered rings are fused into chains parallel to [010]. These chains are interconnected by chains of six-membered rings, extending in the same direction. Two O atoms (O2 and O3ⁱⁱ) from the Zn2O₄ tetrahedron form Zn—O—P bridges, while two symmetry equivalents of three-coordinate O4, which complete the tetrahedron at Zn2, bridge two Zn2 and one P1 congener each. As a result, O4 mediates another set of linkages, namely Zn2^v—O4—Zn2^{viii} and P1—O4—Zn2^v (symmetry codes from Fig. 3). Every Zn—O—Zn bridge in the structure is centred on a three-coordinate O atom. The trigonal coordination of the oxygen bridges is only common in structures with divalent tetrahedral atoms (Bu *et al.*, 1996). The third bond to oxygen in this structure is to P1. In this way, every Zn2 is connected through oxygen to six neighbouring tetrahedral cations (four equivalents of P1 and two of Zn2); and every P1 is linked to five Zn (four Zn2 and one Zn1) (Fig. 3).

The Zn2—O distances are, as expected, shorter for O2 and O3 than for three-coordinate O4 (Table 1). The average Zn2—O bond length is 1.95 (2) Å. The Zn2O₄ tetrahedron, having O—Zn2—O angles ranging between 102.62 (4) and 121.60 (6)°, is somewhat irregular.

The space between layers is occupied by Zn1O₂(N1/O5)₂ tetrahedra. Each Zn1 atom, located on a twofold axis (position 4*e*), is tetrahedrally coordinated by two bridging O atoms [two symmetry equivalents O1 and O1ⁱ; symmetry code: (i) $-x, y,$

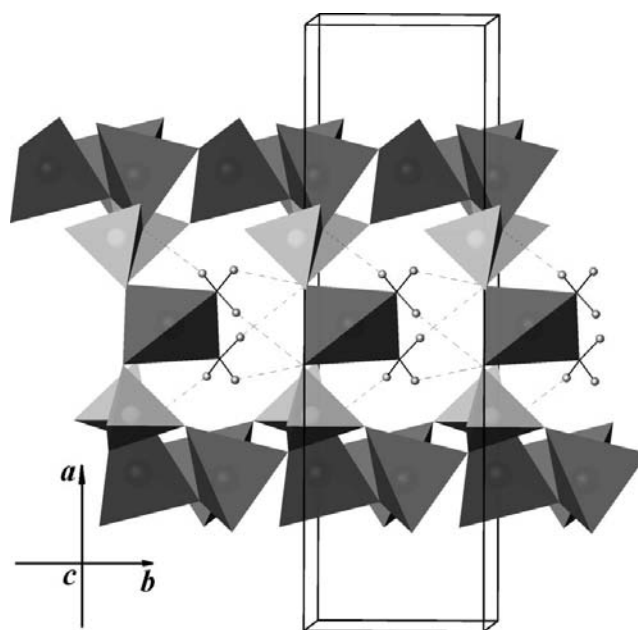


Figure 1
Side view of the boundaries of layers of P1O₄ and Zn2O₄ vertex-sharing tetrahedra with the volume occupied by Zn1O₂(N1/O5)₂ tetrahedra. The H...O contacts are shown as dashed lines and H atoms are shown as small spheres.

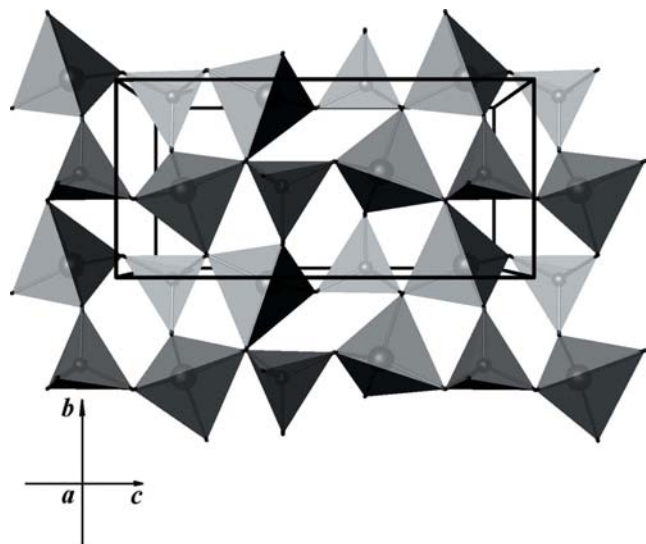


Figure 2

Projection of a single polyhedral layer showing Zn2–O–P1 rings generated from the vertex linking of P1O₄ (smaller) and Zn₂O₄ (larger) tetrahedra.

$-z + \frac{3}{2}$] and by two terminal ligands N1/O5, *i.e.* disordered ammine and water molecules in the ratio 3:2 as established by elemental analysis. O1 and O1ⁱ are bonded to neighbouring P1 atoms forming two Zn1–O1–P1 linkages, thus connecting the Zn1O₂(N1/O5)₂ tetrahedra with the principal *bc* plane layers. The coordination about Zn1 is considerably distorted tetrahedral, with bond angles varying from 97.3 (1) to 117.4 (1)°. P1 exhibits nearly ideal tetrahedral coordination [mean P1–O = 1.54 (1) Å and O–P1–O = 106.0 (1)–112.6 (1)°], with the longest distance P1–O4 involving three-coordinate oxygen (Table 1). The results of bond-valence calculations (Wills, 2009) confirm the presence of divalent zinc and pentavalent phosphorus [calculated values are $\sum v_{ij}(\text{Zn1}) = 2.02$, $\sum v_{ij}(\text{P1}) = 4.97$ and $\sum v_{ij}(\text{Zn2}) = 2.09$ v.u.]. In addition to the Zn1–O1–P1 linkages, N1/O5–H···O hydrogen bonds and other electrostatic contacts provide a connection between the ammine/water sites and the main *bc* plane layers (Table 2).

From the crystallographic and elemental analyses, the ammine and water occupy the same crystallographic site in the ratio 3:2. The ammine molecule is pyramidal and the observed H–N–H angles are in the range 105 (3)–111 (3)°. It is evident that water at this site can have any of three orientations, and it is not possible to establish a model distinguishing among the possibilities, which in any event should be equally probable.

The title compound is isostructural with two compounds, *viz.* the arsenate Be₃(AsO₄)₂·2H₂O (Harrison *et al.*, 1994) and the phosphate Be₃(PO₄)₂·2H₂O (Gier *et al.*, 1999). The incorporation of a larger cation in the structure (As or Zn instead of P or Be, respectively) increases the lengths of the unit-cell axes and decreases β (Table 3). Also, the average *M*–O–*X* (*M* = Be, Zn; *X* = As, P) bond angle of 126.1° in [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}] is 0.9 and 4.7°, respectively, less than the corresponding *M*–O–*X* in Be₃(AsO₄)₂·2H₂O and

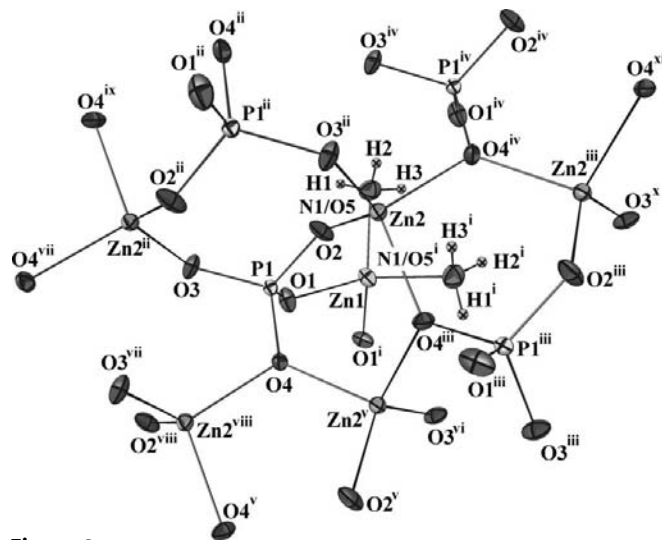


Figure 3

Perspective view of neighbouring P1O₄ tetrahedra in the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radius. [Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, y + 1, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $x, -y, z - \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y - \frac{1}{2}, -z + 2$; (viii) $x, y - 1, z$; (ix) $x, -y, z + \frac{1}{2}$; (x) $x, -y + 1, z - \frac{1}{2}$; (xi) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{3}{2}$]

Be₃(PO₄)₂·2H₂O. Differences in the structures are presumably related to the polyhedral dimensions and different networks of N/O–H···O hydrogen bonds and electrostatic contacts. In the isostructural Be₃(AsO₄)₂·2H₂O and Be₃(PO₄)₂·2H₂O compounds, there are two water molecules available for hydrogen bonding. It was reported that only one H atom is involved in hydrogen bonding, but from our examination of the structures it appears that in both structures all H atoms participate in hydrogen bonding. Two H atoms in Be₃(AsO₄)₂·2H₂O act similarly to H1 and H2 in [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}], while in Be₃(PO₄)₂·2H₂O they are similar to H1 and H3. In all three structures, one of the (N/O)–H groups of each water or water/ammine site is hydrogen bonded to an *M*–O–*X* bridge and forms the strongest hydrogen bond between *MO*₂(N/O)₂ (*M* = Be, Zn) tetrahedra and the *bc* plane layers. The second O–H or (N/O)–H group of each such site forms weak hydrogen bonds in the isostructural Be compounds, but in the title compound the interaction distances to neighbouring *M*1O₂(N1/O5)₂ tetrahedra have expanded to the point that these can be called simply electrostatic contacts. The *D*···*A* distances are in the ranges 2.72–3.18, 2.71–3.16 and 2.977 (3)–3.232 (3) Å for Be₃(PO₄)₂·2H₂O, Be₃(AsO₄)₂·2H₂O and [Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}], respectively. It appears that the influence of As substitution for P on the *D*···*A* distances is weak, but the incorporation of Zn instead of the smaller Be causes a significant increase in the *D*···*A* distances.

Experimental

[Zn₃(PO₄)₂(H₂O)_{0.8}(NH₃)_{1.2}] was synthesized hydrothermally from a mixture of CdO, (NH₄)₂HPO₄ (Loba Chemie 10310 >99%) and 5ZnO·2CO₃·4H₂O (Alfa Products, >99%). The solid mixture was

transferred into a Teflon vessel which was filled to approximately 70% of its inner volume with distilled water. The pH of the mixture was 7. The vessel was enclosed in a stainless steel autoclave, which was heated under autogenous pressure from room temperature to 473 K (4 h), held at this temperature for 72 h and finally cooled to room temperature over a period of 96 h. The resulting products were filtered off, washed thoroughly with distilled water and dried in the air at room temperature. The title compound crystallized as regular colourless plate-like and lath-like crystals (yield 50%) up to 200 μm in length. Qualitative chemical analyses were performed using a JEOL JSM-6400LV scanning electron microscope connected with a LINK energy-dispersive X-ray analysis (EDX) unit. The presence of Zn and P was confirmed in all samples studied. Elemental analysis (H and N) was performed by standard micromethods using an ELEMENTAR Vario EL III C·H·N·S=0 analyzer.

Crystal data

$[\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_{0.8}(\text{NH}_3)_{1.2}]$	$V = 897.2(3) \text{ \AA}^3$
$M_r = 420.90$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.932(3) \text{ \AA}$	$\mu = 8.34 \text{ mm}^{-1}$
$b = 5.0171(10) \text{ \AA}$	$T = 294 \text{ K}$
$c = 10.564(2) \text{ \AA}$	$0.15 \times 0.13 \times 0.08 \text{ mm}$
$\beta = 91.27(3)^\circ$	

Data collection

Nonius KappaCCD diffractometer	1715 measured reflections
Absorption correction: multi-scan (Otwinowski & Minor, 1997)	913 independent reflections
$T_{\min} = 0.298, T_{\max} = 0.513$	884 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.035$	
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
913 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
79 parameters	
5 restraints	

Table 1

Selected bond lengths (\AA).

Zn1—O1	1.9548 (15)	Zn2—O4 ^{iv}	1.9883 (15)
Zn1—N1	2.026 (2)	P1—O1	1.5178 (15)
Zn2—O2	1.9073 (15)	P1—O2	1.5213 (15)
Zn2—O3 ⁱⁱ	1.9091 (15)	P1—O3	1.5294 (14)
Zn2—O4 ⁱⁱⁱ	1.9839 (14)	P1—O4	1.5738 (15)

Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, y + 1, z$.

Table 2

Hydrogen bonds and electrostatic contacts ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1/O5—H1 \cdots O3 ⁱⁱⁱ	0.88 (1)	2.17 (2)	2.977 (3)	151 (3)
N1/O5—H2 \cdots O1 ^{iv}	0.93 (2)	2.39 (3)	3.165 (3)	140 (3)
N1/O5—H3 \cdots O1 ⁱⁱⁱ	0.89 (1)	2.59 (3)	3.232 (3)	130 (3)

Symmetry codes: (iv) $x, y + 1, z$; (xii) $-x, -y, -z + 2$; (xiii) $-x, y + 1, -z + \frac{3}{2}$.

The terminal ligand at Zn1 was refined as a mixed N1/O5 site, constrained to full occupancy and identical fractional coordinates and displacement parameters were used for both atoms. Because the site

Table 3

Unit-cell parameters for three isostructural compounds.

	$\text{Be}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}^a$	$\text{Be}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}^b$	$[\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_{0.8}(\text{NH}_3)_{1.2}]^c$
a (\AA)	15.9640 (6)	16.318 (2)	16.932 (3)
b (\AA)	4.5842 (2)	4.6664 (3)	5.0171 (10)
c (\AA)	9.5320 (4)	9.8755 (7)	10.564 (2)
β ($^\circ$)	94.366 (2)	93.777 (3)	91.27 (3)
V (\AA^3)	695.5 (2)	750.37 (2)	897.2 (3)

References: (a) Gier *et al.* (1999); (b) Harrison *et al.* (1994); (c) this study.

occupancies for N1 and O5 could not be refined independently, they were fixed according to the elemental analysis as N1 0.6 and O5 0.4. Fixed site occupancies of 0.87 were assigned to all three H atoms in order to have their sum fixed at 2.6 H atoms per $(\text{NH}_3)_{0.6}(\text{H}_2\text{O})_{0.4}$ group. All three H atoms were found in a difference Fourier map and refined with restraints [$0.88(2) \text{ \AA}$] on the N1/O5—H distances. $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}(\text{N1/O5})$.

Data collection: COLLECT (Nonius, 2002); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and WinGX (Farrugia, 1999); molecular graphics: ATOMS (Dowty, 2000); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3219). Services for accessing these data are described at the back of the journal.

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