

$(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$, an open-framework structureMaja Mrak,^a Uwe Kolitsch,^{b*}
Venčeslav Kaučič^a and Ekkehart
Tillmanns^b^aNational Institute of Chemistry, Hajdrihova 19,
SI-1000 Ljubljana, Slovenia, and ^bUniversität
Wien, Institut für Mineralogie und
Kristallographie, Geozentrum, Althanstrasse 14,
A-1090 Wien, AustriaCorrespondence e-mail:
uwe.kolitsch@univie.ac.at

Key indicators

Single-crystal X-ray study
 $T = 150 \text{ K}$
Mean $\sigma(\text{P}-\text{O}) = 0.002 \text{ \AA}$
 R factor = 0.023
 wR factor = 0.059
Data-to-parameter ratio = 17.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Ammonium di(zinc, gallium) bis(phosphate), $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$, has a zeolite-like open-framework structure. It contains channels of four- and eight-membered rings of alternating tetrahedra of $(\text{Zn,Ga})\text{O}_4$ ($\text{Zn:Ga} \approx 1:1$) and PO_4 , in which the tetrahedra are connected *via* corners. The NH_4^+ cations are located in the channels and provide weak hydrogen bonds to the framework O atoms. The average $(\text{Zn,Ga})-\text{O}$ bond lengths of the two non-equivalent $(\text{Zn,Ga})\text{O}_4$ tetrahedra are 1.863 and 1.870 Å. All atoms are in general positions. The compound is isostructural with $\text{K}(\text{Co}^{\text{II}},\text{Al})_2(\text{PO}_4)_2$ and $[(\text{NH}_4)_x(\text{NH}_3)_{0.5-x}]\text{Co}_x\text{Al}_{1-x}\text{PO}_4$ ($x = 0.38$). Single-crystal Raman and IR spectra are discussed.

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Comment

The structure of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$ is built up from corner-sharing $(\text{Zn,Ga})\text{O}_4$ and PO_4 tetrahedra. The resulting framework contains intersecting channels which are delimited by four- and eight-membered rings and run parallel to the major axes (Fig. 1). The NH_4^+ cations are located inside the channels (Fig. 1) but provide only weak hydrogen bonds to the framework O atoms. The N site is fully occupied. Semi-quantitative SEM-EDS (Jeol JXA-840A with Tracor software) analyses of the crystal used for the structural study gave a Zn:Ga:P ratio of 1:1:2.

The two non-equivalent $(\text{Zn,Ga})\text{O}_4$ tetrahedra contain equally distributed Zn and Ga atoms with a ratio very close to 1:1 (required by charge balance and confirmed by the chemical analyses). The average $(\text{Zn,Ga})-\text{O}$ bond lengths are 1.863 and 1.870 Å for the $(\text{Zn,Ga})1$ and $(\text{Zn,Ga})2$ sites, respectively. Reported average Zn—O and Ga—O distances for tetrahedrally coordinated Zn and Ga are 1.958 and 1.823 Å, respectively (Baur, 1981). The latter value also coincides with a value of 1.82 Å reported for tetrahedrally coordinated Ga in a recent short literature survey on Ga—O distances in gallophosphate materials (Overweg *et al.*, 1999). (For trigonal-bipyramidally and octahedrally coordinated Ga atoms, average Ga—O distances of ~ 1.89 and ~ 1.96 Å were found, respectively.) Thus, simple interpolation for a Zn:Ga ratio of 1:1 would give an 'ideal' distance of 1.89 Å and would suggest that the Zn:Ga ratio is somewhat lower than 1:1. However, such an interpolation neglects the strong influence of the local site environment of the involved O atoms. In the refinement, the Zn:Ga ratio has been fixed to 1:1, as required by charge balance (see also below for additional evidence from spectroscopic data). Bond-valence sums, calculated using the parameters of Brese & O'Keeffe (1991), give an average value of 2.70 and 2.60 v.u. for the $(\text{Zn,Ga})1$ and $(\text{Zn,Ga})2$ sites, respectively. Calculated values for P1 and P2 are both 4.96 v.u.

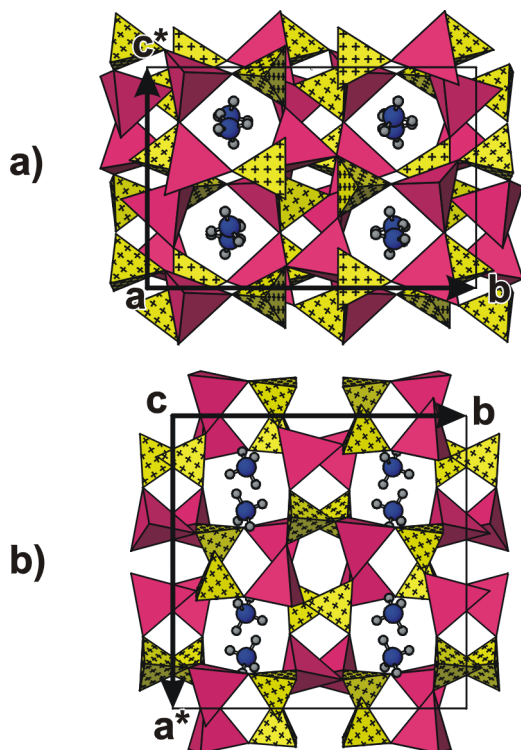


Figure 1
Polyhedral depiction of the open-framework structure of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$ (a) viewed along $[100]$ and (b) viewed along $[001]$. $(\text{Zn,Ga})\text{O}_4$ tetrahedra are red and PO_4 tetrahedra are yellow and marked with crosses. The N atoms of the NH_4^+ cations located in the channels are shown in dark blue.

The agreement between chemical determinations of Zn:Ga ratios and average tetrahedral $(\text{Zn,Ga})\text{—O}$ bond lengths in zinc–gallophosphate materials does not always seem to be good. For example, in $\text{A}[\text{Zn}_3\text{Ga}(\text{PO}_4)_4]\cdot\text{H}_2\text{O}$ [$\text{A} = \text{H}_3\text{DETA} = \text{triprotonated } \text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$] characterized by Lin & Wang (2002), the Zn:Ga ratio in the formula was ‘further confirmed by electron microprobe analysis’. However, the reported average $(\text{Zn,Ga})\text{—O}$ bond length, 1.884 Å, would rather indicate a Zn:Ga ratio very close to 1:1 instead of 3:1. In fact, this would not contradict the observation of Lin & Wang (2002) that the triprotonated DETA template, which balances the negative charge of the framework, is ‘severely disordered and barely no organic moiety could be located.’ Thus, because the overall occupancy of the template could not be refined, its occupancy could, in fact, be less than unity, and the necessary charge balance could be provided by a higher Ga content, *i.e.* a Zn:Ga ratio lower than 3:1.

The framework O atoms O1, O6 and, to a lesser degree, O5 and O4, show a distinctly anisotropic behaviour, strongly vibrating perpendicular to the kinked $(\text{Zn,Ga})\text{—O—P}$ connection (Fig. 2). The three strongest peaks in the final difference-Fourier map are, in fact, at positions most probably representing alternative positions of O1, O6 and O2 with very low respective site occupancies. It must be noted that these strongest peaks are not attributable to H-atom positions, although they could be suspected as such.

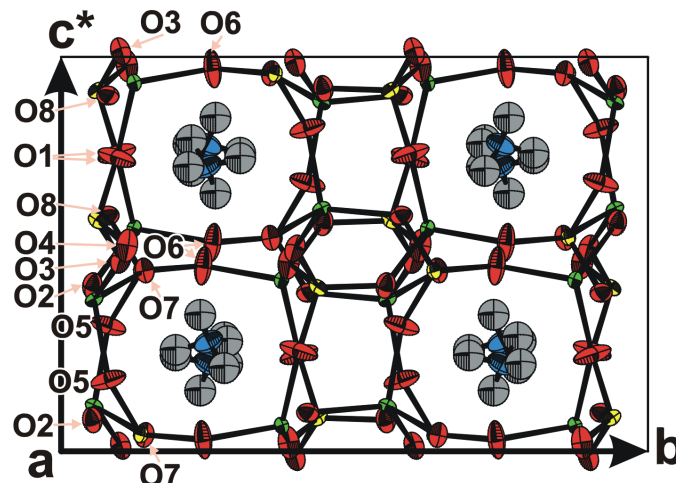


Figure 2
View along $[100]$, showing displacement ellipsoids drawn at the 50% probability level. Atom colours are: $(\text{Zn,Ga}) = \text{green}$, $\text{P} = \text{yellow}$, $\text{O} = \text{red}$, $\text{N} = \text{blue}$, $\text{H} = \text{grey}$. Note the distinct anisotropy of some O atoms (see *Comment*).

The title compound is isostructural with $\text{K}(\text{Co}^{\text{II}},\text{Al})_2(\text{PO}_4)_2$ (Chen *et al.*, 1997) and $[(\text{NH}_4)_x(\text{NH}_3)_{0.5-x}]\text{Co}_x\text{Al}_{1-x}\text{PO}_4$, where x is smaller than or equal to 0.4 (Bontchev & Sevov, 1997; data for $x = 0.38$). The presence of NH_3 groups in the latter was based on the observation that the refinement gave an occupancy ratio $\text{Co}:\text{Al} = 0.38:0.63$ which did not conform to the ratio obtained from ICP chemical analyses [0.24 (8):0.76 and 0.25 (8):0.75 for two runs]; these authors also noted that the refinement of a second crystal gave the site occupancy ratio $\text{Co}:\text{Al} = 0.30:0.70$. The H-atom positions in $[(\text{NH}_4)_x(\text{NH}_3)_{0.5-x}]\text{Co}_x\text{Al}_{1-x}\text{PO}_4$ were not determined, and measured IR data were not discussed in terms of the distinction between NH_4 and NH_3 . In $\text{K}(\text{Co}^{\text{II}},\text{Al})_2(\text{PO}_4)_2$ (Chen *et al.*, 1997), the refined $\text{Co}:\text{Al}$ ratios in the two $(\text{Co,Al})\text{O}_4$ tetrahedra were 0.44:0.56 and 0.48:0.52, *i.e.* close to the ideal ratio of 1:1 required by charge balance.

The refinement of the 150 K data of the title compound provided no evidence of the existence of NH_3 in the tunnels. It was possible to detect all four H atoms of the NH_4 group, and none of them showed any disorder. If part of the NH_4 had been replaced by NH_3 , then one would expect that some or all atoms of the NH_4 group would be somewhat disordered. On the other hand, one might ‘see’ only 60–80% of the H atoms belonging (only) to the NH_4 group.

To provide a better characterization of the formula of the title compound, we also collected single-crystal intensity data at room temperature from the same crystal used for the data collection at 150 K. Furthermore, we measured single-crystal Raman and IR spectra at room temperature.

In the refinement of the room-temperature intensity data, all four H atoms of the NH_4 group could again be located. They showed, as would be expected, somewhat higher isotropic displacement parameters compared to the low-temperature data. The final $R1$ value, 0.025 (for 2207 observed

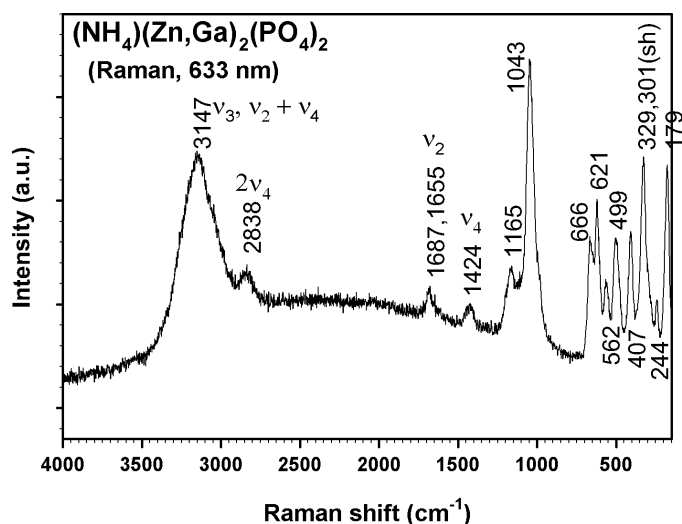


Figure 3
Single-crystal Raman spectrum of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$. Assignments refer to the vibrations of the NH_4 group. Bands below 1200 cm^{-1} are due to vibrations of the PO_4 and $(\text{Zn,Ga})\text{O}_4$ groups and due to lattice modes.

data), is slightly higher than that of the measurement at 150 K.

The single-crystal Raman data were recorded with a Renishaw M1000 MicroRaman Imaging System using a laser wavelength of 633 nm and excitation through a Leica DMLM optical microscope (spectral range 150 to 4000 cm^{-1} , spectral resolution $\pm 2\text{ cm}^{-1}$, minimum lateral resolution $\sim 2\text{ }\mu\text{m}$, random sample orientation). A typical spectrum and band assignments are shown in Fig. 3. The band assignments are based on the well characterized vibrations of the NH_4^+ cation (Nakamoto, 1986). No evidence for the presence of NH_3 molecules was found. A comparison of the spectrum with those of two other ammonium–(zinc,gallium)–phosphates with framework topologies, analcime-type $(\text{NH}_4)_2[\text{Zn}_2\text{Ga}-$

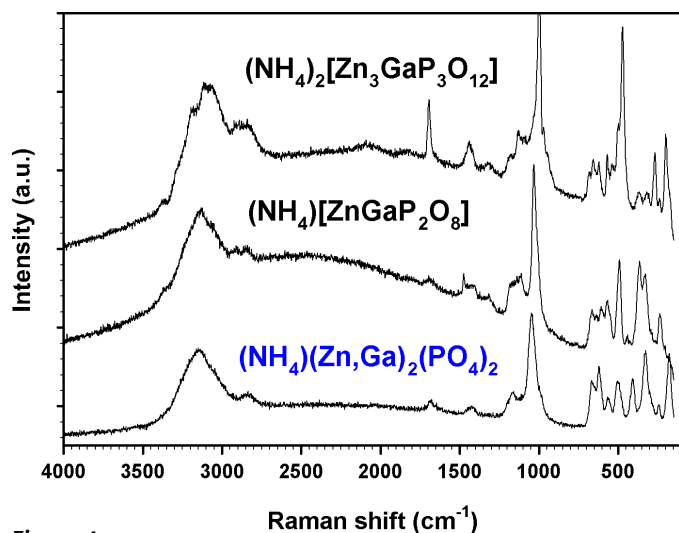


Figure 4
Single-crystal Raman spectrum of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$, compared to those of related ammonium–(zinc,gallium)–phosphates with framework topologies: analcime-type $(\text{NH}_4)_2[\text{Zn}_2\text{GaP}_3\text{O}_{12}]$ and paracelsian-type $(\text{NH}_4)[\text{ZnGaP}_2\text{O}_8]$ (Logar *et al.*, 2001). Note the strong similarities in the range above 1200 cm^{-1} .

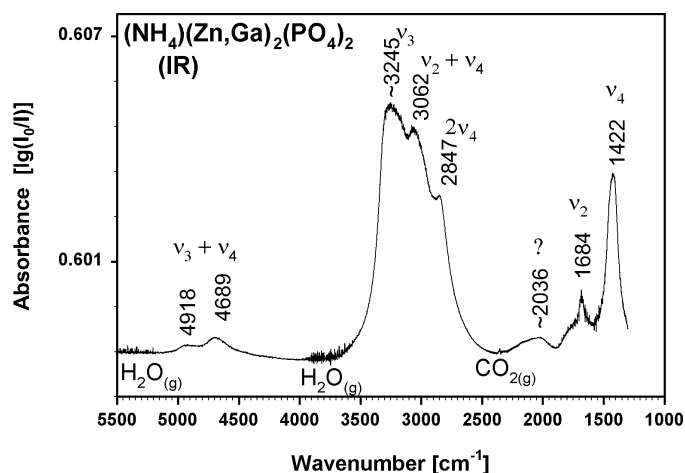


Figure 5
Single-crystal IR spectrum of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$. The spectrum has been cut off below 1300 cm^{-1} because of too high absorption in this region. Assignments refer to the vibrations of the NH_4 group. Note that the (normally forbidden) ν_2 band of the NH_4 group appears to be present in the spectrum, possibly due to the low site symmetry of this group. Spikes due to gaseous H_2O and CO_2 are present, because the spectrum was not measured under vacuum.

$\text{P}_3\text{O}_{12}]$ and paracelsian-type $(\text{NH}_4)[\text{ZnGaP}_2\text{O}_8]$ (Logar *et al.*, 2001) is given in Fig. 4 (all spectra were recorded under identical or similar conditions). The comparison shows that the three spectra are fairly similar in the upper and intermediate wavenumber ranges, especially concerning the bands due to the NH_4 group. Differences at lower wavenumbers are caused by the different character of the individual frameworks, which produce different lattice modes.

The single-crystal IR data were recorded using a Bruker IFS 66v/S FTIR spectrometer with attached microscope (spectral range 1000 to 7500 cm^{-1} , resolution 2.0 cm^{-1} , thin crystal fragment with random orientation). A typical spectrum and band assignments are shown in Fig. 5. The band assignments are based on the well characterized vibrations of the NH_4^+ cation (Nakamoto, 1986) and the detailed analysis of NH_4^+ vibrations in the framework structure of buddingtonite, $(\text{NH}_4)[\text{AlSi}_3\text{O}_8]$ (Harlov *et al.*, 2001). Again, no evidence for the presence of NH_3 molecules was found.

In conclusion, the results of the chemical analyses and of the spectroscopic measurements contradict the bond-valence calculations, which suggest that the Zn:Ga ratio is smaller than 1:1 and there could be small amounts of NH_3 present. Thus, the stoichiometries of the title compound and of $[(\text{NH}_4)_x(\text{NH}_3)_{0.5-x}]\text{Co}_x\text{Al}_{1-x}\text{PO}_4$ (Bontchev & Sevov, 1997) cannot be considered as completely verified and therefore should be further investigated by suitable diffraction methods, such as synchrotron or neutron diffraction, or using specialized spectroscopic techniques. The suggested diffraction studies would also shed more light on the alternative positions of atoms O1, O6 and O2 in the title compound.

The unit-cell volume of $(\text{NH}_4)(\text{Zn,Ga})_2(\text{PO}_4)_2$ ($1560.4\text{ }\text{\AA}^3$) is, owing to the presence of Ga, distinctly larger than that of the Al-members $\text{K}(\text{Co}^{\text{II}},\text{Al})_2(\text{PO}_4)_2$ and $[(\text{NH}_4)_x(\text{NH}_3)_{0.5-x}]\text{Co}_x\text{Al}_{1-x}\text{PO}_4$ (1496.9 and $1533.2\text{ }\text{\AA}^3$, respectively).

The N···O donor–acceptor distances of the hydrogen bonds in the title compound range between 3.005 (4) and 3.050 (4) Å, and are very similar to those in [(NH₄)_x(NH₃)_{0.5–x}]_xCo_xAl_{1–x}PO₄ (Bontchev & Sevov, 1997).

It can be postulated that other phosphates (and possibly arsenates) exist, which are isostructural with the above three phosphate compounds. Hypothetical end-members would be characterized by the following five cation combinations: K–Zn–Al, (NH₄)–Zn–Al, K–Co–Ga, K–Zn–Ga and (NH₄)–Co–Ga. It is noteworthy that the stoichiometrically identical mixed-valence ammonium iron phosphate (NH₄)(Fe^{II},Fe^{III})₂(PO₄)₂ (Boudin & Lii, 1998) has a different framework structure containing PO₄ tetrahedra and chains of edge-sharing Fe^{II}O₆ octahedra, which are connected to chains of corner-sharing Fe^{III}O₆ octahedra. As in the title compound, resulting channels host the NH₄⁺ cations.

An arrangement of tetrahedral rings similar to that in the title compound is encountered in the zeolite structure type APD (AlPO₄–D) (Baerlocher *et al.*, 2001).

In a recent paper, presenting the results of multi-wavelength synchrotron diffraction studies of organically templated (Zn,Ga)-phosphates, Cowley *et al.* (2002) provide strong evidence that no linear relationship exists between the refined metal site occupancies ($M = \text{Zn, Ga}$) and the mean M –O bond lengths in these compounds. Thus, the results of Cowley *et al.* confirm our finding of a ‘discrepancy’ concerning the Zn:Ga ratios.

Experimental

Small colourless pseudo-rhombohedral crystals were obtained as a by-product in the hydrothermal synthesis of Zn–Ga-phosphates ($T = 443 \text{ K}$, 4 d, pH = 4.5) in a teflon container from a gel containing Ga₂O₃, Zn(ac)₂·2H₂O (zinc acetate dihydrate), H₃PO₄, H₂(COO)₂·2H₂O (oxalic acid dihydrate), (CH₃)₄NBr (tetramethylammonium bromide) and water. The crystals were accompanied by analcime- and paracelsian-type NH₄–Zn–Ga-phosphates (Logar *et al.*, 2001), a cancrinite-type Zn–Ga-phosphate presently under study by the authors, and very minor amounts of Zn(C₂O₄)·2H₂O (Giester, 1997).

Crystal data

(NH₄)(Zn,Ga)₂(PO₄)₂
 $M_r = 343.07$
 Monoclinic, $C2/c$
 $a = 13.370 (3) \text{ \AA}$
 $b = 13.190 (3) \text{ \AA}$
 $c = 8.998 (2) \text{ \AA}$
 $\beta = 100.46 (3)^\circ$
 $V = 1560.4 (6) \text{ \AA}^3$
 $Z = 8$

$D_x = 2.921 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 2331 reflections
 $\theta = 2.3\text{--}30.0^\circ$
 $\mu = 6.95 \text{ mm}^{-1}$
 $T = 150 (2) \text{ K}$
 Fragment, colourless
 $0.18 \times 0.11 \times 0.11 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: multi-scan (HKL SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.363$, $T_{\max} = 0.515$
 4483 measured reflections

2287 independent reflections
 2207 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.011$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -18 \rightarrow 18$
 $k = -18 \rightarrow 18$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.059$
 $S = 1.18$
 2287 reflections
 131 parameters
 Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 9.8P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.00 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00097 (13)

Table 1

Selected geometric parameters (Å, °).

Zn1–O3	1.855 (2)	P1–O1 ⁱ	1.517 (3)
Zn1–O8	1.857 (2)	P1–O2 ⁱⁱ	1.520 (2)
Zn1–O5	1.862 (2)	P1–O3 ⁱⁱⁱ	1.528 (2)
Zn1–O7	1.878 (2)	P1–O4	1.532 (2)
Zn2–O1	1.850 (3)	P2–O5 ⁱ	1.514 (2)
Zn2–O4	1.863 (2)	P2–O6	1.518 (2)
Zn2–O6	1.878 (2)	P2–O8 ^{iv}	1.532 (2)
Zn2–O2	1.889 (2)	P2–O7	1.533 (2)
O3–Zn1–O8	117.93 (10)	O1 ⁱ –P1–O2 ⁱⁱ	109.44 (17)
O3–Zn1–O5	104.93 (12)	O1 ⁱ –P1–O3 ⁱⁱⁱ	106.02 (16)
O8–Zn1–O5	107.04 (12)	O2 ⁱⁱ –P1–O3 ⁱⁱⁱ	112.69 (13)
O3–Zn1–O7	102.69 (10)	O1 ⁱ –P1–O4	113.00 (17)
O8–Zn1–O7	112.36 (9)	O2 ⁱⁱ –P1–O4	110.67 (13)
O5–Zn1–O7	111.72 (10)	O3 ⁱⁱⁱ –P1–O4	104.92 (13)
O1–Zn2–O4	121.02 (13)	O5 ⁱ –P2–O6	112.32 (17)
O1–Zn2–O6	103.92 (14)	O5 ⁱ –P2–O8 ^{iv}	108.13 (14)
O4–Zn2–O6	109.93 (10)	O6–P2–O8 ^{iv}	104.93 (14)
O1–Zn2–O2	108.50 (13)	O5 ⁱ –P2–O7	111.32 (13)
O4–Zn2–O2	110.42 (11)	O6–P2–O7	108.99 (12)
O6–Zn2–O2	101.07 (11)	O8 ^{iv} –P2–O7	110.97 (13)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N–H2···O1 ⁱ	0.90 (4)	2.19 (4)	3.045 (4)	160 (5)
N–H3···O6 ⁱⁱ	0.86 (4)	2.28 (4)	3.005 (4)	141 (4)
N–H3···O8 ⁱⁱⁱ	0.86 (4)	2.28 (4)	3.049 (4)	148 (4)
N–H4···O4	0.83 (4)	2.30 (4)	3.050 (4)	151 (5)

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

Data collection: COLLECT (Nonius, 2001); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Shape Software, 1999); software used to prepare material for publication: SHELXL97.

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