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Organically-Templated Zinc Hydrogen Phosphites: Syntheses, Structures and Properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$

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Abstract

The syntheses, crystal structures and some properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$ are reported. These two polymorphs are the first organically-templated hydrogen phosphites. They are built up from vertex-sharing HPO_3 pseudo pyramids and ZnO_3N tetrahedra, where the Zn–N bond represents a direct link between zinc and the neutral 2-cyanoguanidine template. α-$ZnHPO_3 \cdot N_4C_2H_4$ is built up from infinite layers of vertex-sharing ZnO_3N and HPO_3 groups forming 4-rings and 8-rings. β-$ZnHPO_3 \cdot N_4C_2H_4$ has strong one-dimensional character, with the polyhedral building units forming 4-ring ladders. Similarities and differences to related zinc phosphates are discussed. Crystal data: α-$ZnHPO_3 \cdot N_4C_2H_4$, M_r = 229.44, monoclinic, $P2_1/c$, a = 9.7718 (5) Å, b = 8.2503 (4) Å, c = 9.2491 (5) Å, β = 104.146 (1)°, V = 723.1 (1) Å^3, $R(F)$ = 2.33%, $wR(F)$ = 2.52%. β-$ZnHPO_3 \cdot N_4C_2H_4$, M_r = 229.44, monoclinic, $C2/c$, a = 14.5092 (9) Å, b = 10.5464 (6) Å, c = 10.3342 (6) Å, β = 114.290 (1)°, V = 1441.4 (3) Å^3, $R(F)$ = 3.01%, $wR(F)$ = 3.40%.

Introduction

Organically-templated inorganic networks now cover a remarkable range of compositions and structures.[1] Conceptually, these phases are often considered to be built up from three components: the templating organic cation, the metallic cation, and an oxo-anion, with the latter two moieties forming the inorganic framework. A great deal of attention has been paid to the structure-directing role of the organic species,[2] and the structural effect of variously-coordinated cations, such as distorted octahedral vanadium[3] and pyramidal tin(II).[4] Much less exploratory work has been carried out on the oxo-anion part of the inorganic network, and most groups reported so far invariably adopt tetrahedral coordination. In particular, the $[PO_4]^{3-}$ phosphate anion is ubiquitous in these materials.[5] The possibilities of incorporating the phosphorus(III)-containing, pseudo pyramidal, $[HPO_3]^{2-}$ *hydrogen phosphite* group into extended structures templated by inorganic, alkaline earth cations was demonstrated several years ago.[6] In this paper we report the syntheses, crystal structures, and some properties of α- and β-$ZnHPO_3 \cdot N_4C_2H_4$, two polymorphs of zinc hydrogen phosphite templated by 2-cyanoguanidine, **1**. Their similarities and differences to related organically-templated zinc phosphates[7] are briefly noted.

Experimental

Synthesis: 2.52 g (30 mmol) $C_2N_4H_4$ (2-cyanoguanidine or dicyandiamide, Aldrich), 0.81 g (10 mmol) ZnO (Spectrum), 1.70 g (20 mmol) H_3PO_3, 97% (Aesar), and 18.0 g (1 mol) deionized water were combined in a HDPE bottle. This was shaken well and placed in a 70 °C oven for 3 days, after which the contents were filtered hot. The *p*H of the mother liquors was 5. The solid product was washed with water, then methanol, and dried at 70 °C. The yield was 1.86 g of clumped, intergrown, platy crystals of β-$ZnHPO_3 \cdot N_4C_2H_4$ accompanied by one or two gem-like chunks of α-$ZnHPO_3 \cdot N_4C_2H_4$ and some ZnO powder.

The addition of 2.12 g (10 mmol) of $Sr(NO_3)_2$ (Spectrum) to the same reaction mixture treated by the same reaction conditions (final pH 4.0) and work up completely suppressed the formation of β-$ZnHPO_3 \cdot N_4C_2H_4$ and led to 2.60 g of a mixture of large (to 1 mm), faceted, gem-like chunks of α-$ZnHPO_3 \cdot N_4C_2H_4$ and plates of the known strontium zinc hydrogen phosphite phase $SrZn(HPO_3)_2 \cdot 2H_2O$,[6] in roughly 50:50 ratio, based on visual estimation. The distinctive morphologies of the two components allowed for hand sorting of α-$ZnHPO_3 \cdot N_4C_2H_4$ crystals for physical measurements xxx.

Crystal structures: Suitable crystals (for α-$ZnHPO_3 \cdot N_4C_2H_4$, transparent faceted gem, ~0.19 × 0.31 × 0.39 mm; for β-$ZnHPO_3 \cdot N_4C_2H_4$, transparent rod ~0.05 × 0.06 × 0.43 mm) of each compound were selected and mounted on thin glass fibers with cyanoacrylate adhesive. The β form of $ZnHPO_3 \cdot N_4C_2H_4$ is highly prone to twinning and many crystals showing split/smeared reflection profiles were screened and rejected before a suitable specimen was found. Intensity data for each phase were collected on a Bruker SMART 1000 CCD diffractometer (Mo *K*α radiation, λ = 0.71073 Å, $T = 25 \pm 2$ °C) with the aid of the SMART and SAINT software packages[8] as summarised in Table 1.

In both cases, a hemisphere of data was collected in narrow (0.3°)-slice ω-scan mode (for α-$ZnHPO_3 \cdot N_4C_2H_4$ $2° \le 2\theta \le 65°$, for β-$ZnHPO_3 \cdot N_4C_2H_4$ $2° \le 2\theta \le 60°$). Absorption corrections were applied using SADABS[9] with resulting correction factor ranges of 0.569–0.802 for α-$ZnHPO_3 \cdot N_4C_2H_4$ [7305 reflections scanned, 2575 unique (R_{Int} = 0.019),

2222 observed with $I > \sigma(I)$] and 0.457–0.862 for β-$ZnHPO_3 \cdot N_4C_2H_4$ [6288 reflections scanned, 2112 unique (R_{Int} = 0.032), 1728 observed with $I > \sigma(I)$].

The starting positional parameters for the non-hydrogen atoms were located by direct methods[10] in the space groups $P2_1/c$ (No. 14) for α-$ZnHPO_3 \cdot N_4C_2H_4$ and $C2/c$ (No. 15) for β-$ZnHPO_3 \cdot N_4C_2H_4$, which were assumed for the remainder of the crystallographic study. After isotropic refinement, the five hydrogen atom positions for each phase showed up very clearly in difference Fourier maps, and subsequently, their positional and isotropic thermal factors were refined without constraints. The final difference maps were essentially featureless (for α-$ZnHPO_3 \cdot N_4C_2H_4$, min./max. Δρ = –0.32/+0.45 *e* Å^{-3}; for β-$ZnHPO_3 \cdot N_4C_2H_4$, min./max. Δρ = –0.44/+0.67 *e* Å^{-3})

The final cycles of full-matrix least-squares refinement with CRYSTALS[11] using complex, neutral-atom scattering factors included positional and anisotropic thermal factors for all the non-hydrogen atoms and a Larson-type[12] secondary extinction correction. A calculated weighting scheme was applied in each case,[13] and satisfactory convergence was achieved, as summarised in Table 1.

Results

Crystal structure of α-$ZnHPO_3 \cdot N_4C_2H_4$: The final atomic positional and thermal parameters and selected geometrical data are presented in Tables 2 and 3, respectively. The building unit of α-$ZnHPO_3 \cdot N_4C_2H_4$ is shown in Figure 1 and the complete structure in Figure 2.

α-$ZnHPO_3 \cdot N_4C_2H_4$ contains 11 non-hydrogen atoms. The tetrahedrally-coordinated zinc atom is surrounded by three O atoms (also bonded to P) and one N atom, the latter being the nitrile nitrogen[14] of the 2-cyanoguanidine template. The P atom makes three O atom bridges to Zn near neighbours and bonds to one H atom. This tetrahedral, or pseudo-pyramidal, geometry is characteristic of phosphorus(III), and the P–H bond length of 1.23 (2) Å is typical of previous studies.[ref] The three O atoms form Zn–O–P bridges, with θ_{av} = 126.37°. The geometrical parameters for the 2-cyanoguanidnie component of the structure are in good agreement with structural data for molecular complexes involving the same ligand.[14]

To a first approximation the molecule is planar. The refinement makes clear that both guanidine-like[15] terminal nitrogen atoms (N3 and N4) are doubly protonated. Thus, overall, the template is neutral, in accordance with the charge-balancing requirement.

Hydrogen bonding appears to be significant in stabilising this structure. The $N4H_2$ moiety makes two N–H···O bond and templates across an 8-ring in an adjacent zincophosphite layer. The $N3H_2$ group is involved in one N–H···O bond to an adjacent layer and one N–H···N bond, where the acceptor N atom is the imino (N2) nitrogen species on an adjacent pendant 2-cyanoguandine entity associated with the *same* sheet, but displaced in the *c* direction. This type of inter-fragment N_g–H···N_i (g = guanidine, i = imino) bond has been observed in xxx molecular xxx. There are no hydrogen bonding interactions involving the P–H bond, which is expected because the H atom is assumed to be xxx.

The ZnO_3N and HPO_3 building blocks in α-$ZnHPO_3{\cdot}N_4C_2H_4$ combine to yield a structure with strong two-dimensional character (Figure 3) built up from 4-ring and 8-ring loops (i.e., four or eight polyhedral centers, respectively). The three O atoms form the inter-polyhedral links, and the P–H and Zn–N bonds are "terminal." Each 8-ring is templated above and below by hydrogen bonds from organic entities belonging to adjacent sheets. The P–H bonds project into the 8-rings. The ZnO_3N and HPO_3 moieties strictly alternate and the infinite sheets propagate normal to [100]. The minimum and maximum atom-to-atom dimensions of the squashed 8-ring are 4.45 Å and 8.35 Å, respectively.

Crystal structure of β-$ZnHPO_3{\cdot}N_4C_2H_4$: Final atomic positional and thermal parameters and selected geometrical data are presented in Tables 4 and 5, respectively. The building unit of β-$ZnHPO_3{\cdot}N_4C_2H_4$ is shown in Figure 4 and the complete structure in Figure 5.

β-$ZnHPO_3{\cdot}N_4C_2H_4$ contains the same building blocks as the α-polymorph. The tetrahedral zinc atom is surrounded by three O atoms (also bonded to P) and one nitrile N atom. The P atom makes three O atom bridges to Zn near neighbours and bonds to one H atom. The three O atoms form Zn–O–P bridges, with θ_{av} = 128.65°. There are no unusual features associated with the geometry of the organic component of the structure.

In β-$ZnHPO_3 \cdot N_4C_2H_4$, the polyhedral building blocks combine to yield an extended network with strong one-dimensional character (Figure 6) built up from twisted ladders of 4-ring loops, sharing edges. The ZnO_3N and HPO_3 moieties strictly alternate and the chains propagate along [001]. The P–H vertices protrude away from the chains, roughly in the *a* direction, and the 2-cyanoguanidine groups interleave with similar neighbors from an adjacent chain in the [010] direction (Figure xx). Hydrogen bonding is significant in stabilising the [010] inter-chain interactions. Two of the guanidine hydrogen atoms form simple N–H···O links, and H32 partakes in a bifurcated N–H···(O,O) bond. The fourth H atom (H42) is not involved in hydrogen bonding. Thus, the interaction between sheets of chains in the [100] direction is by means of Van der Waals' forces only.

Discussion

α- and β-$ZnHPO_3 \cdot N_4C_2H_4$, the first organically-templated hydrogen phosphites have been successfully prepared as single crystals and characterized. The mild-condition preparation of two polymorphs of 2-cyanoguanidine zinc hydrogen phosphite is typical of the fecundity of hydrothermal synthesis.[ref] Unfortunately, little insight into *how* these phases form by "self assembly" from (presumably) the same constituent building blocks is afforded by these reactions. Clearly the 2-cyanoguanidine species has carried out a templating function in terms of its hydrogen bonding capability,[ref] but the resulting structures bear little resemblance to each other, although, interestingly, their densities are almost identical. The presence of Zn–N(template) bonds is uncommon, but not unprecedented, in organically-templated zincophosphate structures.[ref] The serendipitous use of strontium nitrate as a "magic ingredient" (ref) to redirect the reaction from β-$ZnHPO_3 \cdot N_4C_2H_4$ to α-$ZnHPO_3 \cdot N_4C_2H_4$ has parallels with the use of xx to prepare xxx and xx to prepare xxx in good yield xxx. It is possible that *p*H plays a role xxxx.

The relationship between these phases and organically-templated zinc phosphates built up from an all-tetrahedral network of ZnO_4 and PO_4 units is of some interest. The layer *motif* of α-$ZnHPO_3 \cdot N_4C_2H_4$ can be described in terms of the 4.8^2 sheet topology[ref] as found in various aluminosilicate zeolite structures. Of course, in the zeolite phases, the Zn–N and P–H bonds are replaced by *T*–O–*T*′ (*T* = tetrahedral atom) links and an infinite three-dimensional framework results. However, similar interrupted (by $Zn–OH_2$ and P–OH links) networks based on a 4.8^2 sheet have been seen in zincophosphates such as

The 4-ring ladder *motif* of β-$ZnHPO_3 \cdot N_4C_2H_4$ corresponds closely to similar one-dimensional network structures constructed from ZnO_4 and HPO_4 building blocks observed in phases such as $H_3N(CH_2)_3NH_3 \cdot Zn(HPO_4)_2$,[ref] although in this case the cationic template does not bond directly to zinc. Some gallophosphates (xx) and aluminophosphates (xx) adopt similar chain structures xxx. In all these phases, hydrogen bonding is assumed to be a key feature in stabilising the resulting crystal structure but xxxx

Organically templated zinc hydrogen phosphites have proven to be a rich field and we will report further examples of these phases shortly.

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References

(1) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.

(2) (a) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756. (b) Lewis, D. W.; Willcok, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* (London), **1996**, *382*, 604.

(3) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweizer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43.

(4) Natarajan, S.; Cheetham, A. K. *J. Solid State Chem.* **1998**, *140*, 435.

(5) For example: (a) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, 35, 5603; (b) Loiseau, T.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 416; (c) Natarajan, S.; Eswaramoorthy, M.; Cheetham, A. K.; Rao, C. N. R. *Chem. Commun.* **1998**, 1561; (d) Lii, K.-H.; Huang, Y.-F.; Zima, V.; Huang, C.-Y.; Lin, H.-M.; Jiang, Y.-C.; Liao, F.-L.; Wang, S.-L. *Chem. Mater.* **1998**, *10*, 2599; (e) Leech, M. A.; Cowley, A. R.; Prout, C. K.; Chippindale, A. M. *Chem. Mater.* **1998**, *10*, 451; (f) Francis, R. J.; Drewitt, M. J.; Halasyamani, P. S.; Ranganathachar, C.; O'Hare, D.; Clegg, W.; Teat, S. J. *Chem. Commun.* **1998**, 279; (g) Lu, J. J.; Goh, N. K.; Chia, L. S. *Chem. Commun.* **1998**, 1709. For further examples, see Ref. 1.

(6) Shieh, M.; Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chem.* **1990**, *29*, 958.

(7) For example: (a) Chavez, A. V.; Nenoff, T. M.; Hannooman, L.; Harrison, W. T. A. *J Solid State Chem.* **1999**, *147*, 584. (b) Chidambaram, D.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J Solid State Chem.* **1999**, *147*, 154, and included references.

(8) SMART and SAINT software for area-detector diffractometers, Bruker Analytical X-ray Systems, Madison, Wisconsin, USA (1999).

(9) G. M. Sheldrick, SADABS, program for scaling and correction of area detector data, University of Göttingen, Germany (1997).

(10) G. M. Sheldrick, SHELXS-86 User Guide, University of Göttingen, Germany.

(11) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford.

(12) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(13) Carruthers J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

(14) Batsanov, A. S.; Hubberstey, P.; Russell, C. E.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **1997**, 2667.

(15) Harrison, W. T. A.; Phillips, M. L. F. *Chem. Mater.* **1997**, *9*, 1837.

Figure Captions

Figure 1. Fragment of the α-$ZnHPO_3 \cdot N_4C_2H_4$ structure (50% thermal ellipsoids) showing the atom labelling scheme. Symmetry related atoms are indicated by O1a, etc.

Figure 2. The structure of α-$ZnHPO_3 \cdot N_4C_2H_4$ viewed down [001] with H atoms omitted for clarity. The xxxxx

Figure 3. Detail of the α-$ZnHPO_3 \cdot N_4C_2H_4$ structure showing the infinite sheets of ZnO_3N and HPO_3 groups forming 4-ring and 8-ring loops (all but the nitrile nitrogen of the template molecule have been omitted for clarity).

Figure 4. Fragment of the β-$ZnHPO_3 \cdot N_4C_2H_4$ structure (50% thermal ellipsoids) showing the atom labelling scheme. Symmetry related atoms are indicated by O2a, etc.

Figure 5. The structure of β-$ZnHPO_3 \cdot N_4C_2H_4$ viewed down [xxx].

Figure 6. Detail of the β-$ZnHPO_3 \cdot N_4C_2H_4$ structure showing the infinite chains of ZnO_3N and HPO_3 groups built up from edge-sharing 4-ring ladders (the P–H hydrogen atom and all but the nitrile nitrogen of the template molecule have been omitted for clarity).

Table 1: Crystallographic Parameters

	α-$ZnHPO_3 \cdot N_4C_2H_4$	β-$ZnHPO_3 \cdot N_4C_2H_4$
Empirical formula	$ZnPO_3N_4C_2H_5$	$ZnPO_3N_4C_2H_5$
Formula weight	229.44	229.44
Crystal system	Monoclinic	Monoclinic
a (Å)	9.7718 (5)	14.5092 (9)
b (Å)	8.2503 (4)	10.5464 (6)
c (Å)	9.2491 (5)	10.3342 (6)
β (°)	104.146 (1)	114.290 (1)
V (Å^3)	723.1 (1)	1441.4 (3)
Z	4	8
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
T (°C)	25 ± 2	25 ± 2
λ (Mo $K\alpha$) (Å)	0.71073	0.71073
ρ_{calc} (g/cm^3)	2.11	2.12
μ (cm^{-1})	36.6	35.9
$R(F)$[a]	2.33	3.01
$R_w(F)$[b]	2.52	3.40

[a] $R = 100 \times \Sigma \; | \; |F_o| - |F_c| \; | \; / \; \Sigma \; |F_o|$

[b] $R_w = 100 \times [\, \Sigma \, w \, (|F_o| - |F_c|)^2 \, / \, \Sigma \, w |F_o|^2 \,]^{1/2}$

Table 2: Atomic Parameters for α-$ZnHPO_3 \cdot N_4C_2H_4$

Atom	*x*	*y*	*z*	U_{eq}
Zn1	0.324853(17)	0.10419(2)	0.040809(17)	0.0185
P1	0.51909(4)	-0.16770(4)	0.20810(4)	0.0177
O1	0.36827(12)	0.07882(15)	-0.15002(12)	0.0255
O2	0.37932(12)	-0.07812(15)	0.17323(13)	0.0265
O3	0.42903(12)	0.29992(14)	0.12552(11)	0.0244
N1	0.12630(16)	0.1475(2)	0.0332(2)	0.0355
N2	-0.08053(15)	0.2616(2)	0.10006(17)	0.0307
N3	-0.15055(16)	0.4061(2)	-0.12594(16)	0.0299
N4	-0.25873(16)	0.4467(2)	0.06363(17)	0.0315
C1	0.02752(16)	0.2043(2)	0.05978(19)	0.0273
C2	-0.16286(15)	0.37024(18)	0.01049(17)	0.0226
H1	0.498(2)	-0.299(3)	0.144(2)	0.026(5)
H31	-0.213(3)	0.470(3)	-0.186(3)	0.037(6)
H32	-0.104(3)	0.346(4)	-0.170(3)	0.047(7)
H41	-0.321(3)	0.515(3)	0.004(3)	0.039(6)
H42	-0.272(3)	0.419(3)	0.150(3)	0.045(7)

Table 3: Selected Bond Distances(Å)[a]/Angles(°) for α-$ZnHPO_3 \cdot N_4C_2H_4$

Zn1-O1	1.925(1)	Zn1-O2	1.9305(11)
Zn1-O3	1.9668(11)	Zn1-N1	1.9570(15)
P1-O1	1.5254(11)	P1-O2	1.5167(12)
P1-O3	1.5215(11)	P1-H1	1.23(2)
N1-C1	1.152(2)	N2-C1	1.292(2)
N2-C2	1.346(2)	N3-C2	1.330(2)
N4-C2	1.3198(19)		
O1-Zn1-O2	114.12(5)	O1-Zn1-O3	104.24(5)
O2-Zn1-O3	110.57(5)	O1-Zn1-N1	115.18(6)
O2-Zn1-N1	106.40(6)	O3-Zn1-N1	106.06(6)
O1-P1-O2	112.37(7)	O1-P1-O3	110.48(6)
O2-P1-O3	111.15(6)	O1-P1-H1	107.5(10)
O2-P1-H1	107.1(10)	O3-P1-H1	108.0(10)
Zn1-O1-P1	127.62(7)	Zn1-O2-P1	127.51(7)
Zn1-O3-P1	123.99(7)	Zn1-N1-C1	160.26(16)
C1-N2-C2	118.29(14)	N1-C1-N2	175.24(18)
N2-C2-N3	123.60(14)	N2-C2-N4	117.45(14)
N3-C2-N4	118.94(15)		

N3-H31···O1	0.89(3)	2.07(3)	2.9489(19)	169(2)
N3-H32···N2	0.84(3)	2.37(3)	3.107(2)	147(3)
N4-H41···O3	0.91(3)	2.06(3)	2.963(2)	169(3)
N4-H42···O2	0.87(3)	2.15(3)	2.959(2)	155(3)

[a]For the hydrogen bonds, the four values correspond to the N–H, H···O, N···O separations, and the N–H···O bond angle, respectively.

Table 4: Atomic Parameters for xx-$ZnHPO_3 \cdot N_4C_2H_4$

Atom	*x*	*y*	*z*	U_{eq}
Zn1	0.41873(2)	0.86283(2)	0.04420(3)	0.0257
P1	0.64006(5)	0.96946(5)	0.22141(6)	0.0242
O1	0.56706(15)	0.87209(16)	0.1225(2)	0.0324
O2	0.36863(18)	0.90092(17)	-0.15449(18)	0.0386
O3	0.36674(16)	0.98221(17)	0.13694(18)	0.0340
N1	0.3835(2)	0.6872(2)	0.0709(3)	0.0413
N2	0.37363(19)	0.4705(2)	0.1459(2)	0.0340
N3	0.3792(2)	0.2566(2)	0.1168(3)	0.0460
N4	0.3894(2)	0.3834(2)	-0.0543(3)	0.0416
C1	0.37929(19)	0.5836(2)	0.1014(3)	0.0288
C2	0.38086(19)	0.3719(2)	0.0675(3)	0.0295
H1	0.726(2)	0.931(3)	0.246(3)	0.033(8)
H31	0.370(3)	0.249(3)	0.192(4)	0.038(8)
H32	0.385(4)	0.195(5)	0.066(5)	0.071(13)
H41	0.395(3)	0.320(4)	-0.097(4)	0.05(1)
H42	0.386(3)	0.456(5)	-0.087(5)	0.065(13)

Table 5: Selected Bond Distances(Å)[a]/Angles(°) for xx-$ZnHPO_3 \cdot N_4C_2H_4$

Zn1-O1	1.965(2)	Zn1-O2	1.9178(17)
Zn1-O3	1.9152(17)	Zn1-N1	1.971(2)
P1-O1	1.5269(18)	P1-O2	1.5136(19)
P1-O3	1.5131(17)	P1-H1	1.23(3)
C1-N1	1.146(3)	C1-N2	1.293(3)
C2-N2	1.349(3)	C2-N3	1.322(3)
C2-N4	1.321(4)		
O1-Zn1-O2	107.39(9)	O1-Zn1-O3	110.58(8)
O2-Zn1-O3	110.13(8)	O1-Zn1-N1	107.0(1)
O2-Zn1-N1	109.94(9)	O3-Zn1-N1	111.68(9)
O1-P1-O2	113.39(11)	O1-P1-O3	113.85(11)
O2-P1-O3	109.6(1)	O1-P1-H1	106.1(15)
O2-P1-H1	106.4(15)	O3-P1-H1	107.0(15)
Zn1-O1-P1	130.51(11)	Zn1-O2-P1	127.02(11)
Zn1-O3-P1	128.43(11)	N1-C1-N2	174.8(3)
N2-C2-N3	117.3(2)	N2-C2-N4	124.2(2)
N3-C2-N4	118.4(2)	Zn1-N1-C1	168.8(3)
C1-N2-C2	117.8(2)		

N3-H31···O2	0.84(4)	2.25(4)	2.944(3)	140(3)
N3-H32···O3	0.86(5)	2.41(5)	2.912(3)	118(4)
N3-H32···O1	0.86(5)	2.43(5)	3.186(3)	147(5)
N4-H41···O1	0.82(4)	2.14(4)	2.919(3)	157(4)

[a]For the hydrogen bonds, the four values correspond to the N–H, H···O, N···O separations, and the N–H···O bond angle, respectively (N3–H32 is bifurcated).