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Short Note

APA₂[Zn₃(HPO₄)₄(H₂O)₂], a Layered Zincophosphate Featuring Template-to-Framework N–H···O and “Synergic” Framework-to-Template O–H···N Hydrogen Bonds and C–H···O Interactions (APA = 2-Amino-1-phenyleneammonium, C₆H₉N₂⁺)

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Abstract: The crystal structure of APA₂[Zn₃(HPO₄)₄(H₂O)₂] (APA = 2-amino-1-phenyleneammonium, C₆H₉N₂⁺) (**1**), as prepared by a predominantly non-aqueous synthesis, is described and compared to related compounds. **1** is built up from an alternating array of ZnO₄ and HPO₄ tetrahedra sharing vertices as Zn–O–P bonds to generate infinite anionic sheets. Within these sheets, polyhedral 4-, 6- and 8-rings are apparent. The negative charge of the inorganic layer is balanced by singly-protonated APA template cations and water molecules are also present. The components are linked by N_t–H···O_f, O_f–H···O_w, O_w–H···O_f and O_f–H···N_t (t = template, f = framework, w = water) hydrogen bonds: the last of these represents an unusual framework-to-template interaction. Weak C_t–H···O_f links may also play a role in consolidating the structure. Crystal data: **1** (C₁₂H₂₆N₄O₁₈P₄Zn₃), *M_r* = 834.36, monoclinic, *C2/c* (No. 15), *Z* = 4, *a* = 20.194 (8) Å, *b* = 8.682 (3) Å, *c* = 15.123 (6) Å, β = 91.510 (11)°, *V* = 2650.5 (17) Å³, *R(F)* = 0.048, *wR(F²)* = 0.112.

Keywords: layered zincophosphate; template; hydrogen bonds

1. Introduction

Since they were first reported in 1992 [1,2], the family of organically-templated zincophosphate frameworks (ZnPOs) has grown to encompass over 100 well-determined structures derived from single-crystal data. Hydrogen bonding from the template (typically N–H···O links from a protonated amine) to the framework is a key structure-directing feature of these phases [3], but it is difficult to apply the predictive paradigms of supramolecular chemistry [4] to this area because there are so many synthetic uncertainties.

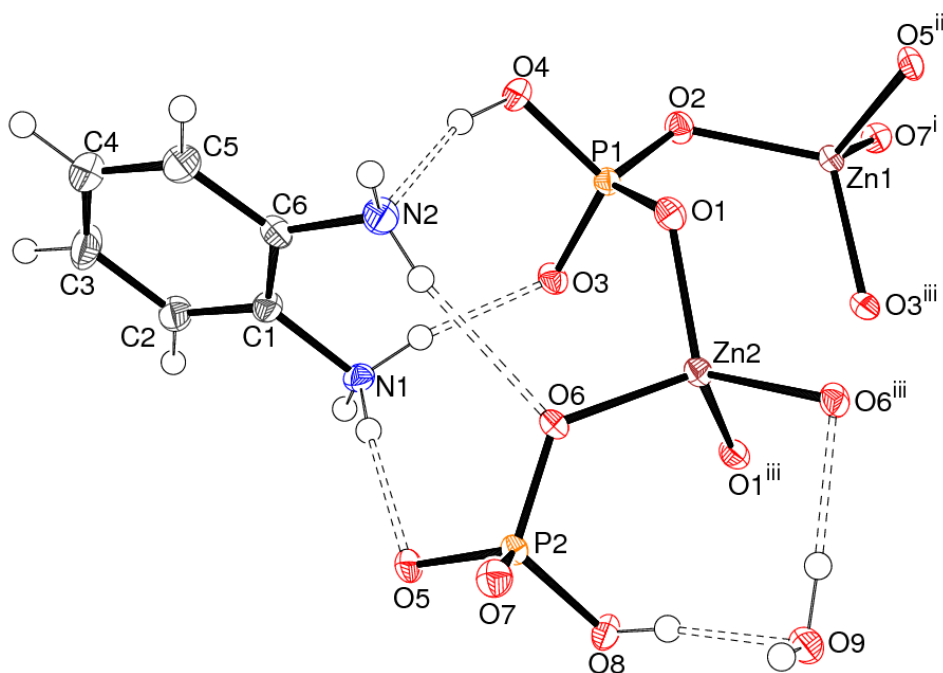
In this short paper we describe the synthesis and crystal structure of $\text{APA}_2[\text{Zn}_3(\text{HPO}_4)_4(\text{H}_2\text{O})_2]$, a layered ZnPO incorporating a new template (APA = 2-amino-1-phenyleneammonium, $\text{C}_6\text{H}_9\text{N}_2^+$), in which some unusual types of hydrogen bond are present.

2. Results and Discussion

Crystal Structure of 1

The asymmetric unit of **1** contains one 2-amino-1-phenyleneammonium cation, two Zn atoms (one of which lies on a crystallographic twofold axis), two $(\text{HPO}_4)^{2-}$ hydrogen phosphate groups and one water molecule of crystallisation (Figure 1). This leads to the 3:4 ratio of Zn:P seen in this compound.

Figure 1. The asymmetric unit of **1** expanded to show the full zinc coordination spheres (50% displacement ellipsoids). The hydrogen bonds are shown as double-dashed lines. Symmetry codes as in Table 2.



Both the zinc atoms in **1** adopt tetrahedral ZnO_4 geometries: mean Zn–O separations of 1.949 Å and 1.947 Å occur for Zn1 and Zn2, respectively. The bond angles around Zn2 (site symmetry 2) are noticeably more distorted from ideal tetrahedral values than those for Zn1: angular variances as defined by Robinson *et al.* [5] of 5.25° (Zn1) and 37.42° (Zn2) arise. The Brown–Altermatt [6] bond

valence sum (BVS) values for Zn1 and Zn2 are 2.07 and 2.08, respectively (expected value = 2.00). All the Zn–O vertices form a bi-coordinate bridge to an adjacent P atom (mean Zn–O–P = 127.3°), thus there are no Zn–O–Zn links in **1**.

The hydrogen phosphate anions possess typical geometrical parameters [7]: mean P1–O = 1.539 Å; O–P1–O angular variance = 4.14°², mean P2–O = 1.536 Å; O–P1–O angular variance = 9.03°². The long P1–O4 and P2–O8 bonds (Table 1) indicate that they are protonated [8], and the H atoms were visible in difference maps. These terminal bonds do not link to zinc atoms. The geometrical parameters for the organic cation in **1** are typical [9].

Table 1. Selected geometrical parameters (Å, °) for **1**.

Bond	Distance	Bond	Distance
Zn1–O7 ⁱ	1.916 (3)	Zn1–O5 ⁱⁱ	1.952 (3)
Zn1–O3 ⁱⁱⁱ	1.962 (3)	Zn1–O2	1.965 (3)
Zn2–O1 ⁱⁱⁱ	1.935 (3)	Zn2–O1	1.935 (3)
Zn2–O6	1.959 (3)	Zn2–O6 ⁱⁱⁱ	1.959 (3)
P1–O1	1.514 (3)	P1–O2	1.527 (3)
P1–O3	1.535 (3)	P1–O4	1.578 (4)
P2–O7	1.506 (4)	P2–O6	1.530 (3)
P2–O5	1.531 (3)	P2–O8	1.577 (3)
Bond	Angle	Bond	Angle
P1–O1–Zn2	119.6 (2)	P1–O2–Zn1	119.3 (2)
P1–O3–Zn1 ⁱⁱⁱ	126.6 (2)	P2–O5–Zn1 ^{iv}	125.7 (2)
P2–O6–Zn2	127.6 (2)	P2–O7–Zn1 ^v	145.2 (2)

Symmetry codes: (i) 1–x, y–1, ½–z; (ii) x, 1–y, z–½; (iii) 1–x, y, ½–z; (iv) x, 1–y, ½+z; (v) 1–x, 1+y, ½–z.

Table 2. Hydrogen-bond geometries (Å, °) for **2**.

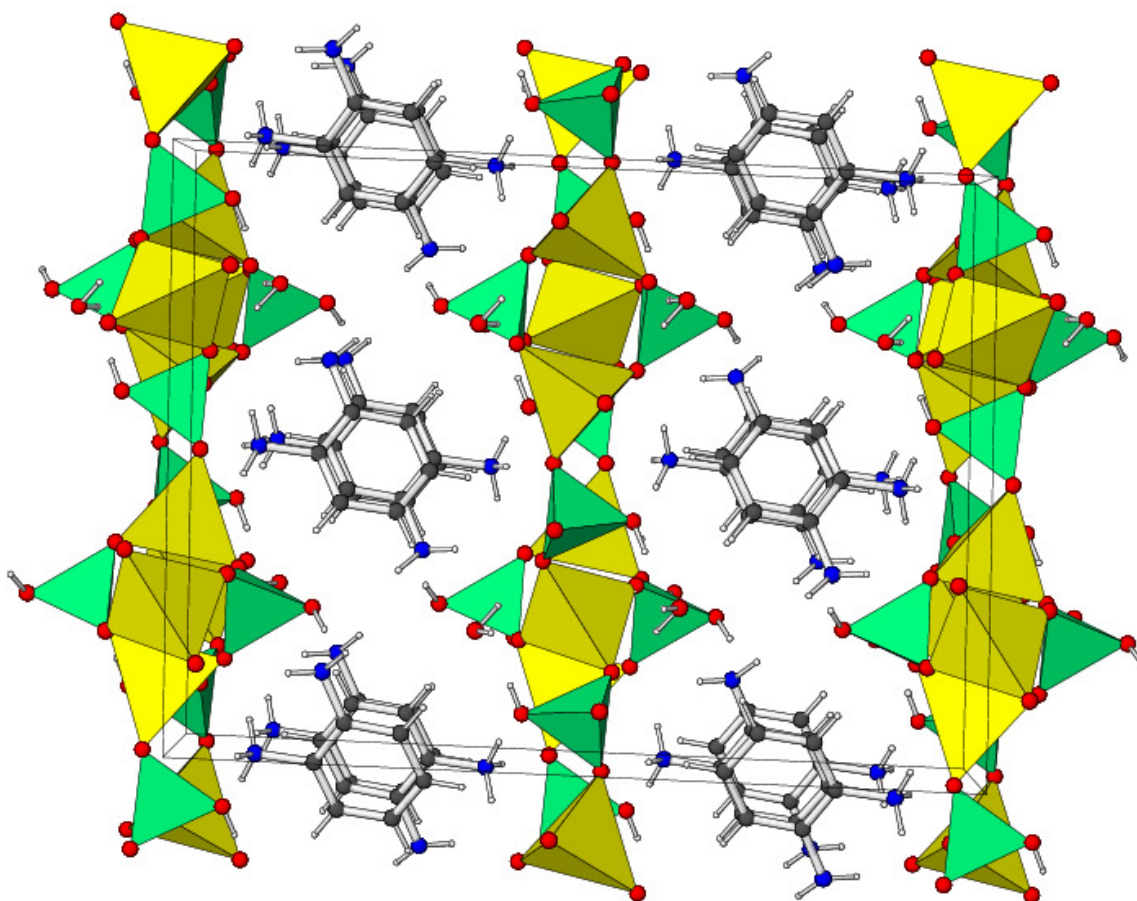
Bond	D–H	H···A	D···A	D–H···A
O4–H1p···N2	1.00	1.86	2.826 (5)	161
O8–H2p···O9	0.83	1.74	2.558 (5)	170
O9–H1w···O6 ⁱⁱⁱ	0.91	1.92	2.819 (5)	170
O9–H2w···O2 ^v	0.88	1.87	2.723 (5)	162
N1–H1a···O3	0.91	1.91	2.803 (5)	166
N1–H1b···O8 ^{vi}	0.91	1.97	2.817 (5)	154
N1–H1c···O5	0.91	1.93	2.825 (5)	166
N2–H2b···O6	0.88	2.30	3.165 (5)	169
C4–H4···O7 ^{vii}	0.95	2.50	3.394 (6)	157
C5–H5···O2 ^{viii}	0.95	2.53	3.421 (6)	157

Symmetry codes: (i) 1–x, y–1, ½–z; (ii) x, 1–y, z–½; (iii) 1–x, y, ½–z; (iv) x, 1–y, ½+z; (v) 1–x, 1+y, ½–z; (vi) 1–x, 1–y, 1–z; (vii) ½–x, 3/2–y, 1–z; (viii) ½–x, ½+y, ½–z.

The connectivity of the Zn- and P-centred building units in **1** leads to infinite sheets of tetrahedra, which propagate in the (100) plane, with the organic cations and water molecules occupying the inter-layer regions (Figure 2). Each Zn node bonds to four different P atoms and each P atom bonds to three different Zn atoms (as well as its terminal P–OH vertex), thus a topological (3,4) net [10] is

formed. The environments of the phosphorus atoms are quite different: pairs of HP1O_4 groups are connected by three ZnO_4 tetrahedra to form distinctive “lantern” motifs, whereas the HP2O_4 groups are linked into pairs bridged by Zn1-centred groups as well as a link to a Zn2 species.

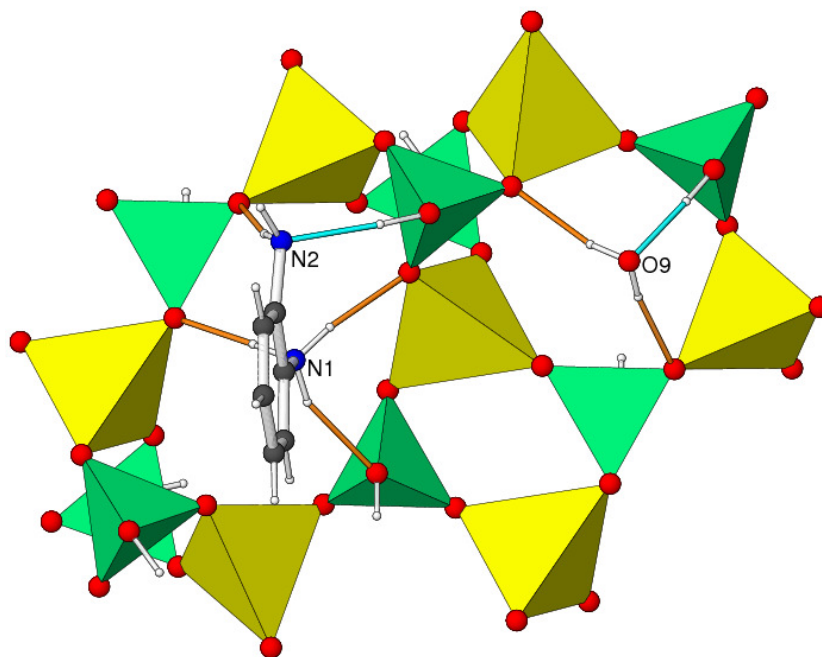
Figure 2. Unit-cell packing for **1** viewed approximately down $[010]$ showing the ZnO_4 and HPO_4 moieties as yellow and green tetrahedra, respectively. Atom colors: O red; N blue; C dark grey; H white.



In terms of polyhedral circuits [11], this connectivity leads to 4-, 6- and 8-ring loops (see Figure 3 below) in the sheets. The 4-ring is a simple grouping of two Zn1- and two P2-centred polyhedra and is generated by inversion symmetry. The 6-ring (generated by twofold rotation symmetry) is more complex and could be described as “bifurcated” [12] due to the presence of a lantern motif in the ring. Finally, the inversion-generated 8-ring contains two lantern motifs as part of its alternating array of Zn- and P-centred polyhedra. As discussed below, these different rings seem to strongly correlate with the hydrogen bonds present in this structure.

Hydrogen bonds are an important feature of most organically-templated networks [13] and the various interactions in **1** are summarised in Table 2. Atom N1 of the APA cation is protonated (as an NH_3^+ group) and forms two $\text{N-H}\cdots\text{O}$ links to bridging O atoms and one link to a terminal P–OH group. All these O atoms occur within one particular (100) sheet, *i.e.*, there are no inter-sheet $\text{N-H}\cdots\text{O}$ links. Based on the short (<2.0 Å) $\text{H}\cdots\text{O}$ separations and large $\text{N-H}\cdots\text{O}$ angles ($>150^\circ$), we may assume that these hydrogen bonds are relatively strong.

Figure 3. Detail of the structure of **1** showing the framework polyhedral 4-, 6-, and 8-rings and the hydrogen-bond interactions (polyhedral and atom colors as in Figure 2). The $N_t-H\cdots O_f$ and $O_w-H\cdots O_f$ (t = template, f = framework, w = water) hydrogen bonds are highlighted in orange; the $O_f-H\cdots O_w$, and $O_f-H\cdots N_t$ links are shown in light blue. Crystal symmetry generates another cation and water molecule below the plane of the tetrahedra with the same hydrogen bonding patterns but these are not shown for clarity.



The situation for the un-protonated N2 group is quite different. This forms one weak (based on its much longer $H\cdots O$ separation of 2.30 Å) $N-H\cdots O$ link to a bridging O atom in the same sheet as the acceptor O atoms for the N1 bonds (Figure 1). Its other H atom does not form a hydrogen bond and points into the inter-layer region. An unusual feature of **1** is the presence of a *framework-to-template* $O-H\cdots N$ hydrogen bond arising from the P1–O4H group, which points towards the region of the presumed lone-pair of electrons of atom N2 (Figure 1).

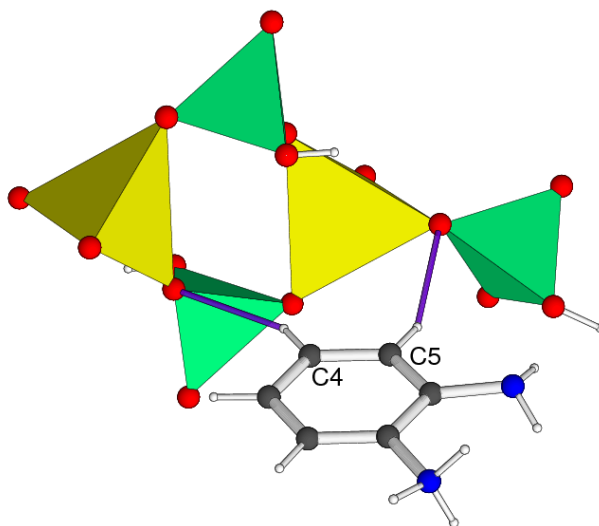
The P2–O8H group forms an $O-H\cdots O$ hydrogen bond to the water molecule and the water molecule in turn forms two $O-H\cdots O$ hydrogen bonds to framework O atom. Again, these framework atoms are in the same (100) sheet. In terms of the graph-set notation of Bernstein *et al.* [14], the smallest circuits involving the $N1H_3^+$ and $N2H_2$ moieties are $R^2_2(10)$ and $R^2_2(8)$ loops, respectively, whereas the water molecule is involved in an $R^2_2(8)$ loop.

These hydrogen bonds appear to exert a significant template effect, as shown in Figure 3. The polyhedral 8-ring is templated by no fewer than eight $N-H\cdots O$ links (four each from the two symmetry-related cations lying to either side of the inorganic sheet) as well as an $O-H\cdots N$ “back bond” from a framework P–OH grouping to each of the template N-atoms. Each O atom in the ring accepts one hydrogen bond. The 6-ring is templated by a pair of water molecules (one above the plane of the framework and one below) but again P–OH \cdots O framework-to-water hydrogen bonds consolidate this effect.

It is notable that there are no classical hydrogen bonds that provide *inter-layer* connectivity in this phase, *i.e.*, as a topological $L\cdots T\cdots L$ linkage [15], which is commonly seen in layered ZnPOs

templated by linear-chain, protonated diamines [16]. However, two C–H···O bonds (Table 2, Figure 4) may provide this cohesion in **1**: there is no ambiguity in the location of the aromatic C–H atoms in question and the H···O separations (around 2.50 Å) and C–H···O angles (>150°) fall well within the accepted criteria for such “non-classical” bonds [17]. Conversely, there are no aromatic π – π stacking interactions in **1**, as the shortest centroid–centroid separation is over 4.24 Å.

Figure 4. Detail of the structure of **1** showing the possible template-to-framework C–H···O interactions (highlighted in purple). The polyhedral and atom colors are as in Figure 2.



3. Experimental Section

Compound **1** was prepared from zinc nitrate, 1 M orthophosphoric acid, 1,2-phenylenediamine with ethylene glycol as a solvent, in a 1:1:1:20 ratio of reactants. Zinc nitrate was added to the 1,2-phenylenediamine in a conical flask before the addition of the ethylene glycol solvent. Finally, the orthophosphoric acid was added to the flask, which was then transferred to a hotplate and stirred for approximately one hour. The reaction mixture was transferred to a plastic bottle, sealed and placed in an 80 °C oven for 24 hours. The solid product was recovered by Büchner filtration and was washed with water and then acetone to yield a mass of colorless prisms of **1**.

The single-crystal data for **1** (colorless prism 0.05 × 0.05 × 0.02 mm) were collected using a Rigaku Mercury CCD diffractometer (graphite monochromated Mo K α radiation, $\lambda = 0.71073$ Å) at –180 °C with the aid of the CrystalClear program. A total of 7634 data were collected to $2\theta_{\max} = 56.6^\circ$ ($-19 \leq h \leq 24$, $-10 \leq k \leq 9$, $-17 \leq l \leq 18$). An empirical (multi-scan) absorption correction was applied at the data reduction stage (2401 merged reflections, $R_{\text{int}} = 0.054$) and the structure was solved by direct methods with SHELXS-97. The resulting atomic model was developed and refined against $|F|^2$ with SHELXL-97 [18] and the “observed data” threshold (encompassing 2192 reflections) for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$.

The C-bound H atoms were placed in idealised locations (C–H = 0.95 Å) and refined as riding atoms. The N-bound H atoms were located in a difference map: those attached to N1 were relocated to idealised locations (N–H = 0.91 Å) and refined as riding; those attached to N2 were refined as riding in their as-found relative locations. The O-bound H atoms were located in difference maps and refined as

riding in their as-found relative locations. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. The final structure was analysed and validated with PLATON [19]. Key crystallographic parameters are listed in Table 3 and full refinement details are given in the deposited cif. IR (cm^{-1}): 3370, 3294 (N–H stretch); 1612 (N–H bend); 1273 (C–N); 590, 540, 441 (framework).

Table 3. Crystallographic parameters for **1**.

Empirical formula	$\text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_{18}\text{P}_4\text{Zn}_3$
M_r	834.36
Temperature (K)	93 (2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
a (Å)	20.194 (8)
b (Å)	8.682 (3)
c (Å)	15.123 (6)
β (°)	91.510 (11)
V (Å ³)	2650.5 (17)
Z	4
ρ_{calc} (g cm ⁻³)	2.091
μ (mm ⁻¹)	3.024
$F(000)$	1680
Data/restraints/parameters	2401/0/187
Goodness-of-fit on F^2	1.065
$R(F)$ [$I > 2\sigma(I)$]	0.048
$wR(F^2)$ (all data)	0.112
Min., max. $\Delta\rho$ ($e \text{ \AA}^{-3}$)	−0.88, +1.29
CSD Deposition number	CCDC-876420

4. Conclusions

The synthesis and crystal structure of $\text{APA}_2[\text{Zn}_3(\text{HPO}_4)_4(\text{H}_2\text{O})_2]$ have been described. This compound appears to be the first zincophosphate to be templated by a protonated aromatic amine, although a zincophosphate network containing $(\text{HPO}_3)^{2-}$ anions [20] has been templated by the doubly-protonated *para*-isomer of the singly-protonated *ortho*-diamine used here. The predominantly non-aqueous synthesis of **1** is uncommon although it is not the first to report the use of ethylene glycol as solvent in preparing a ZnPO [21].

Compound **1** contains the expected polyhedral building units of ZnO_4 and HPO_4 tetrahedra sharing vertices as Zn–O–P links and the polyhedral connectivity results in infinite layers. The “dangling” P–OH bond cannot form a link to zinc, and the topological (3,4) net is the result. The topological similarity of a hydrogen phosphate (HPO_4^{2-}) and a phosphite (HPO_3^{2-}) group in terms of network formation has already been noted [10]. The templating effect of the $\text{C}_6\text{H}_9\text{N}_2^+$ cation in **1** appears to be quite distinctive, with all its “classical” N–H \cdots O hydrogen bonds from the adjacent NH_3^+ and NH_2 groups forming links to a single 8-ring window in the ZnPO layer. As described above, a “synergic” framework-to-template O–H \cdots N bond also occurs, to reinforce the template-to-framework bonds.

Conversely, the water molecule templates a 6-ring aperture in the layer, but again a bond from the framework to the water molecule appears to facilitate this. In terms of bridging the inorganic layers, there are no classical hydrogen bonds in **1**, but two C–H···O interactions are present.

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