# 'Template cooperation' effect leading to 18-ring cavities in the open-framework guanidinium zincophosphate $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$

**William T. A. Harrison***[a]† **and Mark L. F. Phillips**[b]

[a] *Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia*
[b] *Sandia National Laboratories, Albuquerque, NM 87145, USA*

**The novel open-framework phase $(CN_3H_6)_3Zn_7(H_2O)_4$-$(PO_4)_6{\cdot}H_3O$ contains well ordered trios of guanidinium cations cooperating to template 18-ring cavities.**

Zincophosphates (ZnPOs) and phosphonates are now a well established family of framework phases.[1–8] Here, we describe the solution-phase synthesis‡ and single-crystal structure§ of $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$, a novel three-dimensional, open-framework guanidinium zinc phosphate. Our initial thought in terms of 'designer synthesis' was that the distinctive, symmetrical 'propeller' shape of the guanidinium cation might lead to templating of medium-sized rings, with the guanidinum species lying approximately in the plane of the ring, and hydrogen-bonding to framework O atoms, akin to the same cation's behaviour in combination with molecular crown ether compounds.[9] Instead, *three* $(CH_3H_6)^+$ cations 'cooperate' in 'side-on' conformation to template a novel open-framework structure enclosing large 18-ring cavities interconnected by 12-ring windows.

Of the 20 asymmetric non-hydrogen atoms (3 Zn, 2 P, 11 O, 1 C, 3 N) in $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$, 16 belong to the ZnPO framework and four are guests. The framework of the structure is built up from $ZnO_4$, $ZnO_3(H_2O)$ and $PO_4$ tetrahedra, sharing vertices, as Zn–O–P bonds, the Zn–$OH_2$ bonds being 'terminal' (Fig. 1). Zinc- and phosphorus-centred tetrahedra alternate, and there are no Zn–O–Zn bonds in the structure, despite the fact that the Zn : P ratio of the framework exceeds unity. Zn(1) [$d_{av}$ = 1.928(9) Å] makes four bonds to adjacent phosphorus atoms, whilst Zn(2) [$d_{av}$ = 1.982(9) Å] and Zn(3) (site symmetry 3) [$d_{av}$ = 1.95(1) Å] both have one water molecule in their coordination spheres. The two distinct phosphorus centres both make four P–O–Zn bonds to four different adjacent zinc atoms with $d_{av}$(P–O) values of 1.531(9) and 1.519(9) Å for P(1) and P(2), respectively. The framework oxygen atoms O(1)–O(7) and O(9) bond to both Zn and P with $\theta_{av}$ = 129.5°; O(8) and O(10) are oxygen atoms of water molecules and O(20) is an extraframework hydronium cation. Overall, a 7 : 6 Zn : P ratio results for this framework, in contrast to most other zincophosphate phases which are phosphorus rich. Terminal Zn–$OH_2$ units have been previously observed in framework zincophosphates templated by 1,4-diazabicyclo[2.2.2]octane,[10,11] but their structures are completely different from that of $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$. The guanidinium cation [$d_{av}$(C–N) = 1.34(3) Å] makes probable hydrogen-bonding interactions to O atoms of the framework from each of its $NH_2$ 'arms', suggesting that the usual 'delocalised' model of this cation[9] is appropriate for this structure.

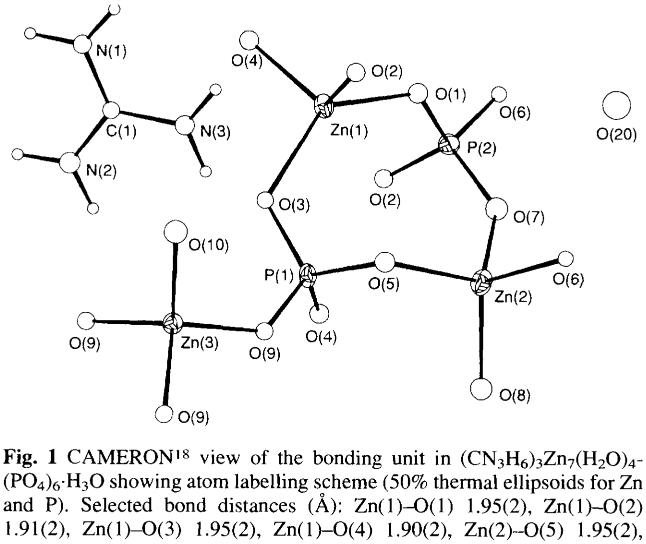

**Fig. 1** CAMERON[18] view of the bonding unit in $(CN_3H_6)_3Zn_7(H_2O)_4$-$(PO_4)_6{\cdot}H_3O$ showing atom labelling scheme (50% thermal ellipsoids for Zn and P). Selected bond distances (Å): Zn(1)–O(1) 1.95(2), Zn(1)–O(2) 1.91(2), Zn(1)–O(3) 1.95(2), Zn(1)–O(4) 1.90(2), Zn(2)–O(5) 1.95(2), Zn(2)–O(6) 1.96(1), Zn(2)–O(7) 1.99(2), Zn(2)–O(8) 2.03(2), Zn(3)–O(9) × 3 1.94(2), Zn(3)–O(10) 1.99(3), P(1)–O(3) 1.54(2), P(1)–O(4) 1.55(2), P(1)–O(5) 1.52(2), P(1)–O(9) 1.51(2), P(2)–O(1) 1.53(2), P(2)–O(2) 1.53(2), P(2)–O(6) 1.50(2), P(2)–O(7) 1.52(2), C(1)–N(1) 1.33(3), C(1)–N(2) 1.34(3), C(1)–N(3) 1.34(3).

The polyhedral connectivity in $(CN_3H_6)_3Zn_7(H_2O)_4$-$(PO_4)_6{\cdot}H_3O$ leads to helical [0001] columns of 4-rings of Zn(1)-, P(1)- and P(2)-centred building units. The 'nodes' of this 4-ring chain are the Zn(1) atoms, with one P(1) and one P(2) atom forming the bridging 4-ring between each zinc centre. This bonding situation is somewhat similar to the helical 4-ring stacks found in the chiral framework of $NaZnPO_4{\cdot}H_2O$.[4] In $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$, these [0001] 4-ring stacks are crosslinked by both the Zn(2)- and Zn(3)-centred units. Zn(2) makes oxygen-bridged bonds to a P(1) and a P(2) species in the same 4-ring chain, resulting in a tetrahedral-atom 4 = 1 bridge (Fig. 2) in the notation of Meier and Olson,[12] which to our knowledge, has not been observed previously in zincophosphate structures. In aluminosilicate zeolites, the 4 = 1 *motif* is associated with 'fibrous' zeolites such as edingtonite,[13] whose structures are completely different to that of $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$. The $Zn(3)O_3(OH_2)$ group in $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$ bridges to a P(1) atom in three different 4-ring chains. Symmetry dictates that the water molecules [O(8)] attached to the Zn(2) species all point in the same direction; likewise for the water molecule [O(10)]

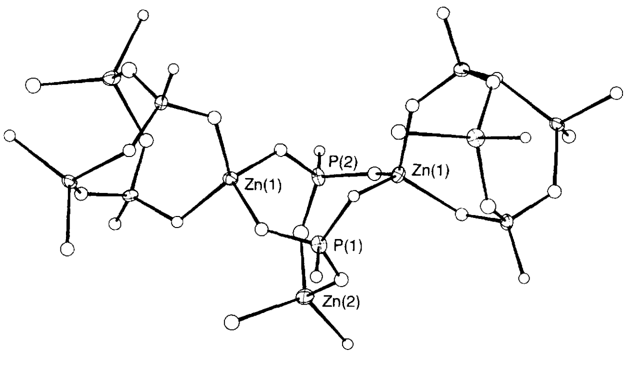

**Fig. 2** View of a chain of side-by-side 4 = 1 units in $(CN_3H_6)_3Zn_7$-$(H_2O)_4(PO_4)_6{\cdot}H_3O$; the chain propagates in the [0001] direction

attached to Zn(3), but these Zn(3)–O(10) vectors are orientated in the opposite sense to the Zn(2)–$OH_2$ groups.

The most striking features of the resulting structure are large cavities located perpendicular to the [0001] direction, surrounded by 18-ring windows (Fig. 3). All five of the framework tetrahedral atoms participate in this ring. These 18-rings may be described as 'bifurcated',[14] *i.e.* one may trace a split path around the 18-ring at three symmetry-equivalent locations where the helical 4-ring columns and the 18-ring intersect. The 18-rings are occupied by *three* well-ordered guanidinium cations, located approximately edge-on relative to the 18-ring. The water molecules attached to Zn(2) and Zn(3) project from above and below into this cavity. The 18-rings are interconnected by distorted 12-ring windows (Fig. 4) aligned roughly perpendicular to [0100] and equivalent directions. The rhombohedral crystal symmetry precludes any infinite channels in this structure; rather, the 18-ring cavities are connected in a staggered fashion. The framework density[12] (number of tetrahedral framework atoms in 1000 Å$^3$) for this material is 15.1, indicating a comparable degree of openness to molecular sieves such as AlPO-52.[15] Other guanidinium zinc phosphates adopt different, novel structures, and will be described later.

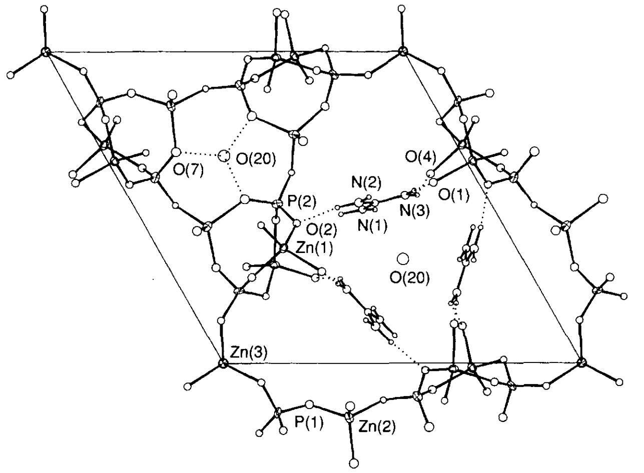

**Fig. 3** View down [0001] of a slice of the $(CN_3H_6)_3Zn_7(H_2O)_4$- $(PO_4)_6{\cdot}H_3O$ structure (*ca.* 0.2 < *z* < *ca.* 0.8) showing the 18-ring cavity occupied by three guanidinium cations, with possible hydrogen-bonding links indicated by dotted lines. A trio of 4 = 1 tetrahedral units linked so as to form a 6-ring is also visible. The hydronium cation [O(20)] occupies a site above this 6-ring, with possible hydrogen-bonding links indicated by dotted lines.

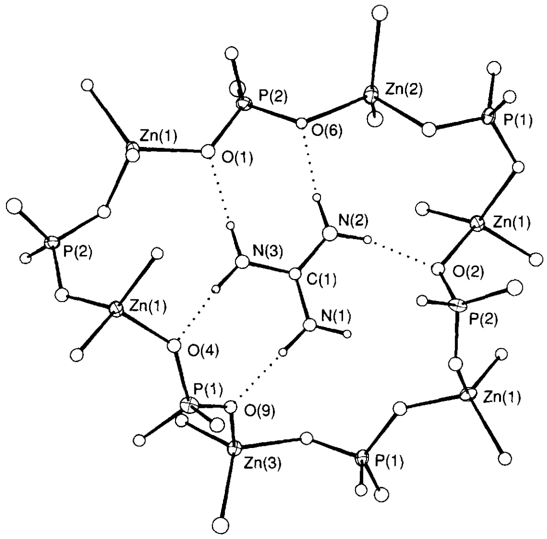

**Fig. 4** View approximately down [0100] of an inter-cavity 12-ring window, with possible template–framework hydrogen-bonding links indicated by dotted lines

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## Footnotes

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† E-mail: wtah@chem.uwa.edu.au

‡ *Synthesis*: $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$ was prepared by mixing 0.60 g $(CN_3H_6)_2CO_3$ (Kodak), 0.76 g 85% $H_3PO_4$ (Fisher), and 10.51 g deionized water in a 100 ml PTFE bottle: 0.814 g ZnO (St Joseph's) was added, shaken well, and allowed to stand at room temperature for 1 day prior to being heated to 100 °C in an oven for 5 days (starting guanidinium : Zn : P ratio *ca.* 2 : 3 : 2). Upon cooling, the crystalline product was recovered from the supernatant liquors by filtration. The product (yield 1.52 g) contained a substantial amount of unreacted zinc oxide powder in addition to some small (up to 0.2 mm maximum linear dimension) transparent rods of the title compound.

§ *Crystal data* for $(CN_3H_6)_3Zn_7(H_2O)_4(PO_4)_6{\cdot}H_3O$: $C_3H_{29}N_9O_{28}P_6Zn_7$, $M_r$ = 1282.81, trigonal, space group *R*3 (no. 146), $a$ = 15.356(6), $c$ = 12.617(4) Å, $U$ = 2576.8(5) Å$^3$, $Z = 3$, $D_c$ = 2.48 g cm$^{-3}$, $\mu$ = 53.15 cm$^{-1}$, $T$ = 298(2) K, $R$ = 0.048, $R_w$ = 0.047 $\{w = 1/[\sigma(F)]^2\}$, $S$ (goodness of fit) = 2.33, crystal dimensions *ca.* 0.05 × 0.05 × 0.2 mm, Siemens P4 automated diffractometer (graphite-monochromated Mo-K$\alpha$ radiation, $\lambda$ = 0.710 73 Å), $2 < 2\theta < 60°$, 1018 data collected, empirical absorption correction based on $\psi$ scans (min. 0.56, max. 0.71), 711 reflections considered observed $[I > 3\sigma(I)]$ after merging ($R_{int}$ = 0.056), structure solution by direct methods,[16] refinement using CRYSTALS.[17] Due to a poor data : parameter ratio, only the Zn and P atoms were refined anisotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/278.

## References

1 T. E. Gier and G. D. Stucky, *Nature*, 1991, **349**, 508.
2 T. Song, M. B. Hursthouse, J. Chen, J. Xu, K. M. A. Malik, R. H. Jones, R. Xu and J. M. Thomas, *Adv. Mater.*, 1994, **6**, 679.
3 W. T. A. Harrison, T. E. Gier, J. M. Nicol and G. D. Stucky, *J. Solid State Chem.*, 1995, **114**, 249.
4 W. T. A. Harrison, R. B. Broach, R. A. Bedard, T. E. Gier and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 145.
5 W. T. A. Harrison, R. B. Broach, R. A. Bedard, T. E. Gier, X. Bu and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 691 and references therein.
6 T. Song, J. Xu, Y. Zhao, Y. Yue, Y. Xu, R. Xu, N. Hu, G. Wei and H. Jia, *J. Chem. Soc., Chem. Commun.*, 1994, 1171.
7 C. Bhardwaj, H. Hu and A. Clearfield, *Inorg. Chem.*, 1993, **32**, 4294.
8 S. Drumel, P. Janvier, D. Deniaud and B. Bujoli, *J. Chem. Soc., Chem. Commun.*, 1995, 1051.
9 J. W. H. M. Uiterwijk, S. Harkema, J. Geevers and D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.*, 1982, 200.
10 W. T. A. Harrison, T. E. Gier, T. E. Martin and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**, 175.
11 W. T. A. Harrison, T. M. Nenoff, M. M. Eddy, T. E. Martin and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**, 1127.
12 W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd edn. (revised), Butterworth-Heinmann, London, 1992.
13 E. Galli, *Acta Crystallogr., Sect. B*, 1976, **32**, 1623.
14 W. T. A. Harrison, T. M. Nenoff, T. E. Gier and G. D. Stucky, *J. Solid State Chem.*, 1994, **113**, 168.
15 J. M. Bennett, R. M. Kirchner and S. T. Wilson, *Proc. 8th International Zeolite Conference*, Elsevier, Amsterdam, 1989, p. 731.
16 G. M. Sheldrick, SHELXS86 User Guide, University of Göttingen, Germany.
17 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, UK.
18 L. M. Pearce, C. K. Prout and D. J. Watkin, CAMERON User Guide, Chemical Crystallography Laboratory, University of Oxford, UK.

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