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Poly[piperazinium(2+) [hexa-μ-hydrogen phosphito-μ-piperazine-pentazinc(II)]]

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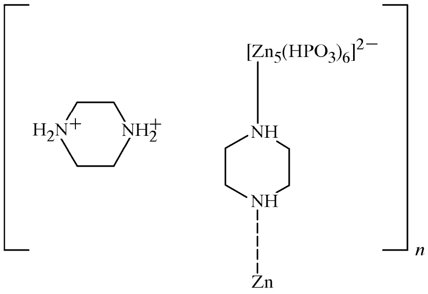
The title compound, $\{(C_4H_{12}N_2)[Zn_5(HPO_3)_6(C_4H_{10}N_2)]\}_n$ contains ZnO_4, ZnO_3N and HPO_3 polyhedral building units linked by Zn—O—P bridges (mean Zn—O—P = 133.6°). The organic species exists in two forms, *i.e.* as neutral molecules that bond directly to zinc as ligands *via* both N atoms and as diprotonated cations that interact with the framework by way of N—H···O hydrogen bonds. Both organic components lie across centres of inversion.

Comment

The title compound, (I), complements the growing family of organically templated zinc–hydrogen phosphite networks (Rodgers & Harrison, 2000; Harrison, 2001; Dong *et al.*, 2003; Lin *et al.*, 2004).



(I)

As shown in Fig. 1, there are five distinct Zn atoms in (I). Three of these metal ions are bonded to four O-atom neighbours in a tetrahedral geometry, and two (Zn4 and Zn5) are bonded to three O atoms and one N atom, the latter atom being part of a piperazine molecule. The mean Zn—O bond length [1.935 (3) Å] is typical for this family of phases (Harrison, 2001), and the Zn—N bonds (Table 1) are also characteristically longer (Kirkpatrick & Harrison, 2004) than the Zn—O links.

The six P atoms all form the centres of tetrahedral $[HPO_3]^{2-}$ anions. Because the P—H vertex of this species does not participate in chemical bonds, the shape of this group is often described as pseudo-pyramidal. The mean P—O bond length in (I) [1.516 (3) Å] and the narrow range of P—O distances [1.498 (3)–1.532 (3) Å] is normal (Lin *et al.*, 2004).

The 18 O atoms in (I) all exist as Zn—O—P bridges, with a mean bond angle of 133.6° [range 123.30 (17)–144.69 (19)°]; thus, in (I) there are no terminal or 'dangling' P═O or P—OH bonds, like those seen in some related phases (Harrison, 2001). Also, there are no Zn—O—Zn or P—O—P bridges in (I).

The organic species exists in both neutral and diprotonated forms in (I). There are four distinct half-molecules in the asymmetric unit (two neutral and two protonated). The four complete molecules are generated by inversion symmetry in every case and the resulting molecular conformations are typical six-membered-ring chairs. The neutral piperazine molecules (containing atoms N1 and N2) form ligand-like bonds to Zn atoms from both their N atoms, *i.e.* they act as framework bridges (Ritchie & Harrison, 2004). The Zn atoms

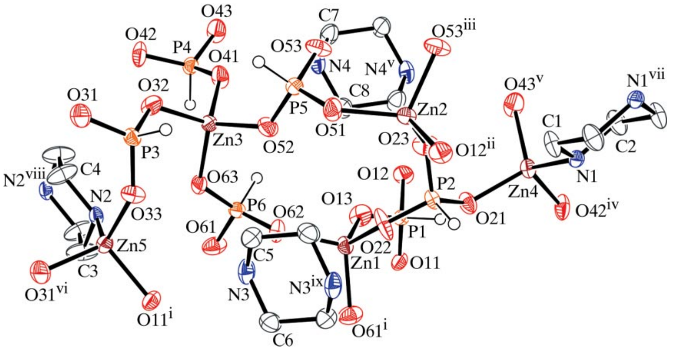


Figure 1
A fragment of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms; C- and N-bound H atoms have been omitted for clarity). [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+2, -y+1, -z+2$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, -z+2$; (vi) $-x+2, -y, -z+1$; (vii) $-x+2, -y+2, -z+2$; (viii) $-x+1, -y, -z+1$; (ix) $-x+2, -y+1, -z+1$.]

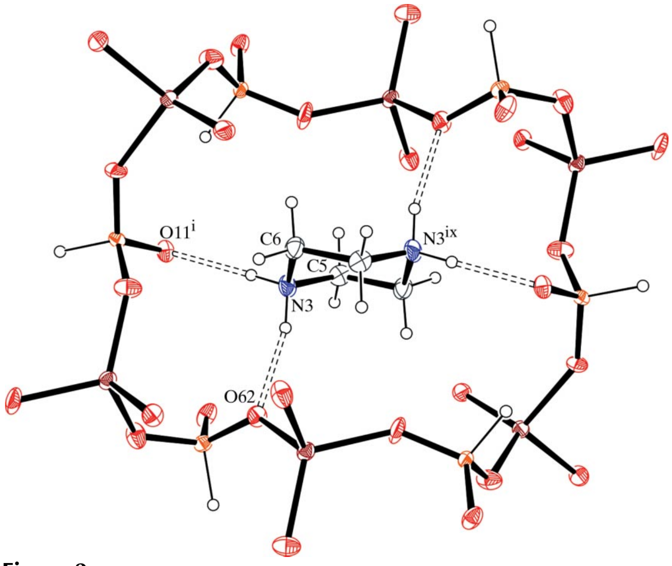


Figure 2
The environment of the N3-containing piperazinium cation in (I), with hydrogen bonds shown as dashed lines. For symmetry codes, see Fig. 1. The N4-containing cation has a similar environment.

are in equatorial positions with respect to the six-membered ring, and the axial H atoms form N—H$\cdots$O hydrogen bonds (Table 2).

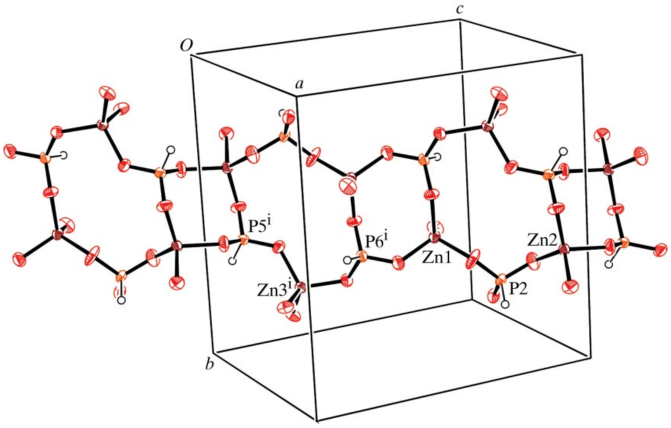


Figure 3
Part of an inorganic chain in (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. Symmetry codes are as in Fig. 1.

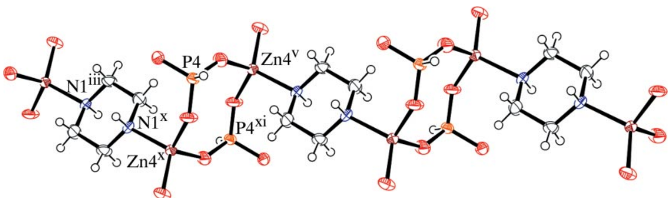


Figure 4
Part of a hybrid chain in (I), showing 50% probability displacement ellipsoids and arbitary spheres for the H atoms. [Symmetry codes: (iii) $-x+2, -y+1, -z+2$; (v) $-x+1, -y+1, -z+2$; (x) $x, y-1, z$; (xi) $-x+1$, $-x+1, -y, -z+2$.] The chain involving the Zn5 and P3 polyhedra and the N2-containing piperazine molecule is very similar.

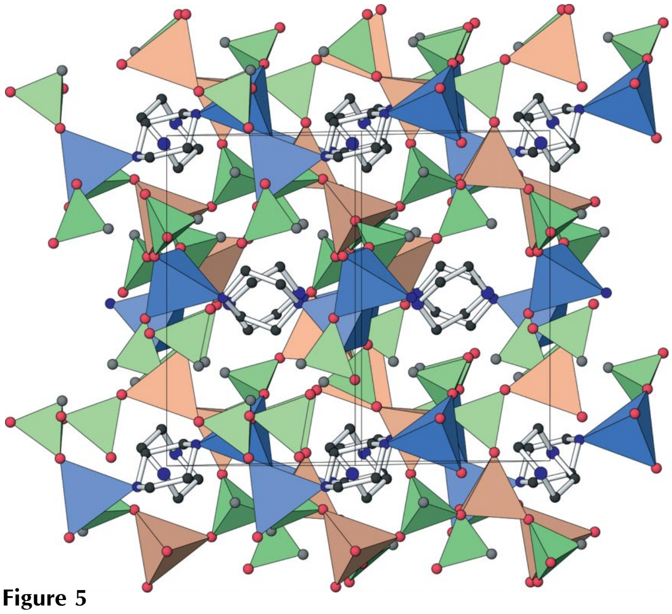


Figure 5
A polyhedral representation of the unit-cell packing for (I), with C- and N-bound H atoms omitted for clarity.

The two diprotonated piperazinium ions (containing atoms N3 and N4) interact with the zincophosphite network by way of N—H$\cdots$O hydrogen bonds. Each N atom makes two N—H$\cdots$O bonds [mean H$\cdots$O = 1.97, mean N$\cdots$O = 2.816 (4) Å and mean N—H$\cdots$O = 159°] and occupies a polyhedral 12-ring (Fig. 2).

The complex structure of (I) can be decomposed into several distinctive subunits. However, the description presented here certainly is not intended to imply that these subunits necessarily play a well defined stepwise role in the formation of (I) from small atomic/molecular units in solution. Firstly, the Zn1-, Zn2-, Zn3-, P2-, P5- and P6-centred polyhedra combine to form chains of alternating polyhedral six- (*i.e.* three ZnO_4 tetrahedra + three HPO_3 pseudo-pyramids) and four-rings propagating in the [101] direction (Fig. 3). In turn, the P1 phosphite groups link to atoms Zn1 and Zn2, and thus crosslink the [101] chains into an infinite (010) sheet.

Considered in isolation, the Zn4- and P4-centred polyhedra and the N1-containing piperazine ring form a distinctive hybrid organic/inorganic chain propagating in [100]. The chain consists of inversion-symmetry-generated four-rings (two Zn4 + two P4), bridged by the piperazine molecules (Fig. 4). The Zn5 and P3 groups and the N2-containing piperazine species form a very similar chain that also propagates in the [100] direction. These two chains alternate with respect to the *c* direction.

When these subunits are conceptually assembled together, a complex three-dimensional framework results. There are lacunae in the hybrid organic/inorganic network that accommodate the N3- and N4-containing diprotonated piperazinium cations as described above. When viewed down [110], there appear to be channels present in the framework (Fig. 5). However, it is notable that, in every channel, the ligand-like and protonated organic species alternate; thus, it is extremely unlikely that the hydrogen-bonded piperazinium species could be removed without drastic changes in the hybrid framework.

Compound (I) complements several other piperazinium zinc phosphites, including $(C_4H_{12}N_2)[Zn_6(HPO_3)_8]\cdot 2H_3O$ (Dong *et al.*, 2003), $(C_4H_{12}N_2)[Zn3(HPO_3)_4]$ (Lin *et al.*, 2004) and $(C_4H_{12}N_2)[Zn(HPO_3)_2]$ (Shi *et al.*, 2004). These are more conventional templated networks in which the protonated organic species interacts with the inorganic network by way of N—H$\cdots$O bonds (Cheetham *et al.*, 1999). Thus, as seen for other templating species, a wide variety of templated networks can arise (Kirkpatrick & Harrison, 2004) for the same combination of metal, oxo-anion and template depending on synthesis conditions. Compound (I) is particularly notable for the dual role – as a framework bridge and as a protonated template – played by the organic species.

Experimental

A mixture of ZnO (0.814 g, 10 mmol), H_3PO_3 (0.820 g, 10 mmol), piperazine hexahydrate (0.971 g, 5 mmol) and water (20 ml) was sealed in a plastic bottle and heated to 353 K for five days. After cooling to room temperature, colourless rods and blocks of (I) were recovered by vacuum filtration and washing with water and acetone.

Crystal data

$(C_4H_{12}N_2)[Zn_5(HPO_3)_6(C_4H_{10}N_2)]$
$M_r = 981.01$
Triclinic, $P\overline{1}$
$a = 8.8634$ (4) Å
$b = 12.6390$ (6) Å
$c = 12.8768$ (6) Å
$\alpha = 89.182$ (1)°
$\beta = 89.913$ (1)°
$\gamma = 86.941$ (1)°
$V = 1440.31$ (12) Å^3
$Z = 2$
$D_x = 2.262$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4175 reflections
$\theta = 2.2$–$30.0°$
$\mu = 4.52$ mm^{-1}
$T = 293$ (2) K
Rod, colourless
$0.13 \times 0.07 \times 0.06$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\rm min} = 0.583$, $T_{\rm max} = 0.763$
16520 measured reflections
8229 independent reflections
5216 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\rm max} = 30.0°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.077$
$S = 0.90$
8229 reflections
370 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.59$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn4—N1	2.065 (3)	Zn5—N2	2.042 (3)

H atoms were located in difference maps and then placed in idealized locations (P—H = 1.32 Å, C—H = 0.97 Å, and N—H = 0.90 and 0.91 Å) and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(carrier).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O32$^{\rm iv}$	0.91	2.12	2.993 (4)	160
N2—H2$A\cdots$O63	0.91	2.15	2.967 (4)	150
N3—H3$A\cdots$O11$^{\rm i}$	0.90	1.93	2.799 (4)	163
N3—H3$B\cdots$O62	0.90	1.96	2.841 (5)	165
N4—H4$A\cdots$O53	0.90	2.10	2.853 (5)	141
N4—H4$B\cdots$O41	0.90	1.89	2.772 (4)	168

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (iv) $x, y+1, z$.

We thank Laura Gordon for experimental assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3006). Services for accessing these data are described at the back of the journal.

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