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$[Zn_3(HPO_4)_4](NMe_4)_2$: a zincophosphate containing interruptions of isolated hydrogen-bonding $[H–O(P)]_4$ groupings within a novel three-dimensional four-connected framework

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The new zincophosphate $[Zn_3(HPO_4)_4](NMe_4)_2$, **I**, has been synthesized hydrothermally, and the crystal structure was determined by single-crystal X-ray diffraction. Corner-sharing ZnO_4 and $PO_3(OH)$ tetrahedra form zigzag ladder chains of edge-sharing 4-membered rings. These chains link into the anionic host framework that, formally, generates a three-dimensional system of intersecting channels bound by 16-membered rings, in which tetramethylammonium cations reside. However, the channels are partly blocked by hydrogen bonds in $[H–O(P)]_4$ groupings. Formal substitution of the four H atoms in each grouping by a tetravalent cation results in a fully four-connected network of equal charge and novel topology that generates gismondine-type $[4^68^4]$ cavities at the intersections of 8-membered ring channels. **I** was further studied by variable-temperature powder X-ray diffraction, thermogravimetry, and FT-IR spectroscopy.

Introduction

A great number of inorganic open-framework microporous materials[1a] (*e.g.* metallophosphates) have been synthesized and modified in view of their established or potential applications in traditional fields (*e.g.*, separation, heterogeneous catalysis)[1b] as well as in new fields[1c] (*e.g.*, nonlinear optics,[1d] microlasers,[1e] microswitches,[1f] artificial antenna systems,[1g] photoluminescent materials,[1h] chemical sensors[1i]). Among these materials, open-framework zincophosphates belong to the most intensively studied systems, and a rich diversity of crystal structures has been found. Recently, the possibility of self-assembly of particular low-dimensional inorganic units to complex open-framework zincophosphates has been considered,[2] and the first *in situ* studies aimed at gaining insight into the mechanisms of structure formation have been undertaken.[3] Interesting are, for example, organically-templated three-dimensional interrupted framework zincophosphates with extra-large channels bound by 20- and 24-membered rings.[4] In phosphates with divalent metal cations, such as the zincophosphate system, three-dimensional four-connected zeolite-type materials are expected to be produced only when small cations with high charge density are used as templates in the synthesis due to the host–guest charge-density matching principle.[5]

Here, we report on the synthesis and single-crystal X-ray structure of the open-framework zincophosphate $[Zn_3(HPO_4)_4](NMe_4)_2$, **I**. This new material deserves attention due to the existence of isolated hydrogen bonding $[H–O(P)]_4$ groupings in a four-connected host framework of novel topology that is related to the zeolite gismondine structure. Additionally, **I** was studied by variable-temperature powder X-ray diffraction (XRD), thermogravimetry (TG), difference thermal analysis (DTA), and infrared (IR) spectroscopy.

Experimental

Syntheses and methods of characterization

I was first obtained in exploratory hydrothermal syntheses designed for novel organically-templated zincoborophosphates. After having solved the X-ray structure and therefore recognized the stoichiometry, the material was prepared in the absence of the boron source (H_3BO_3).

A typical synthesis recipe was as follows: 3.86 g phosphoric acid (85 wt% in water) was placed in a glass beaker. 6.16 g tetramethylammonium hydroxide pentahydrate and 1.33 g zinc oxide were successively added under stirring. For homogenization the white suspension of molar composition $NMe_4OH : H_3PO_4 : ZnO : H_2O = 2.1 : 2.0 : 1.0 : 12.4$ (pH *ca.* 8) was heated under continuous stirring until a viscous gel resulted. The hot gel was transferred into a Teflon-lined stainless steel autoclave of 8 ml volume (degree of filling 40%) and kept at 463 K under static conditions and autogenous pressure for 4 days. The white product was filtered off, washed with small amounts of deionized water and dried in a vacuum at room temperature. The mother liquor had a pH of 7.5. The crystals obtained were up to 0.3 mm in size, generally not well-faceted and apparently frequently twinned.

Powder XRD revealed that the product contained **I** along with a very small amount of other, as yet not identified, crystalline material. We have not succeeded in preparing **I** completely single-phase. A common by-product in the syntheses of **I** was a known zincophosphate, $[Zn(HPO_4)(H_2PO_4)](NMe_4)$,[6] the formation of which could be avoided by employing the method described above. Two further tetramethylammonium zincophosphates have been reported in the literature.[7] Extensive washing of **I** with water at room temperature results in the transformation of the compound into hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$).

Room-temperature powder XRD patterns were recorded on a Huber G670 Guinier diffractometer with image foil detector using $CuK_{\alpha1}$ radiation. A variable-temperature powder XRD photograph of **I** was taken on a Guinier camera using $CuK_{\alpha1}$ radiation. A powdered sample was kept in an unsealed Quartz-glass capillary and heated in an air atmosphere up to 1173 K at a rate of 0.3 K min^{-1}. TG/DTA measurements were performed on a Netzsch STA 429 thermoanalyzer in a flowing oxygen atmosphere up to 1303 K using heating rates of 5 K min^{-1}. FT-IR spectra were recorded on a BioRad Digilab Division FTS-60 spectrometer between 400 and 4000 cm^{-1} using KBr pellets.

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Single-crystal X-ray diffraction studies

A suitable crystal, 0.22 × 0.21 × 0.16 mm^3 in size, was glued to the tip of a glass fibre. All X-ray measurements were done on an Enraf-Nonius CAD4 diffractometer at room temperature using graphite-monochromatized MoK_α radiation. Empirical absorption corrections on the basis of ψ-scans were applied. For structure solution and refinement the SHELXS97 and SHELXL97 program systems were used.[8]

H atoms of methyl groups were geometrically constructed and treated riding on the respective C atoms. The coordinates of the disordered H atom of the terminal P–OH group (O4 atom) could be determined by Fourier difference syntheses. These H-atom positions were refined with the O–H distances being restrained to 0.90(2) Å, and fixed isotropic displacement parameters.

Crystal data and further information about the structure determination are collected in Table 1. Table 2 lists the refined atomic parameters.

CCDC reference number 170511. See http://www.rsc.org/suppdata/jm/b1/b106274n/ for crystallographic files in .cif format.

Results

The open-framework zincophosphate **I** has been synthesized for the first time under mild hydrothermal conditions using tetramethylammonium cations as template species.

Table 1 Crystal data and details of structure analysis for $[Zn_3(HPO_4)_4](NMe_4)_2$ (**I**)

Empirical formula	$C_8H_{28}N_2O_{16}P_4Zn_3$
Formula weight	728.32
Crystal system	Orthorhombic
Space group; Z	*Fddd*; 8
a/Å	9.203(1)
b/Å	15.776(2)
c/Å	31.587(4)
V/Å^3	4586(1)
T/K	293
μ/mm^{-1}	3.469
ρ_{calc}/mg·mm^{-3}	2.110
Reflections measured	3519
Unique reflections, total; R_{int}	1668; 0.056
Unique reflections, $I > 2\sigma_I$	1040
Parameters refined	83
R_1[a] [$I > 2\sigma_I$]	0.037
wR_2[b] [all data]	0.087
Largest diff. peak, hole/e·Å^{-3}	+0.93, −0.55

[a] $R_1 = \Sigma(|F_{obs}| - |F_{calc}|)/\Sigma|F_{obs}|$. [b] $wR_2 = [\Sigma[w(F^2_{obs} - F^2_{calc})^2]/\Sigma[w(F^2_{obs})^2]]^{0.5}$.

Table 2 Final refined coordinates[a] and equivalent isotropic displacement parameters (Å^2) for $[Zn_3(HPO_4)_4](NMe_4)_2$ (**I**)

Atom	x	y	z	U_{eq}[b]/U_{iso}
Zn(1)	−0.1250	0.3750	0.3750	0.0182(2)
Zn(2)	−0.1250	0.3750	0.23928(2)	0.0183(2)
P	0.1018(1)	0.30470(6)	0.30866(3)	0.0160(2)
O(1)	0.0525(3)	0.3563(2)	0.27112(9)	0.0284(7)
O(2)	−0.0128(3)	0.2943(2)	0.34228(9)	0.0287(7)
O(3)	0.1713(3)	0.2219(2)	0.29649(8)	0.0279(7)
O(4)	0.2279(3)	0.3593(2)	0.33108(9)	0.0317(7)
H(1)[c]	0.319(4)	0.359(7)	0.321(3)	0.050
H(2)[c]	0.181(9)	0.355(7)	0.356(2)	0.050
N	0.3750	0.3750	0.1841(1)	0.028(1)
C(1)	0.250(1)	0.3932(8)	0.1593(3)	0.169(5)
C(2)	0.349(1)	0.3026(5)	0.2091(3)	0.199(7)

[a] Origin on inversion centre (origin choice 2) of space group *Fddd*. [b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [c] Statistically half-occupied position.

Crystal structure

Strictly alternating ZnO_4 and $PO_3(OH)$ tetrahedra are linked *via* common corners into the three-dimensional anionic host framework (Fig. 1) with typical bond lengths and angles: Av. (Zn–O) = 1.941 Å, av. (P–O) = 1.532 Å, av. (Zn–O–P) = 136.0°. The framework charges are balanced by tetramethylammonium cations which rest as guest species in the void system. The Zn(1) atom lies at a site with 222 (D_2) crystallographic symmetry, the Zn(2) atom and the N atom of the organic cation lie at sites with 2-fold (C_2) symmetry. All but one unique O atom are two-connected [Zn–(μ_2-O)–P bridges]. The O(4) atom belongs to a terminal P–OH group with an expectedly long P–O(4) bond length of 1.609 Å.

The most obvious infinite structural units in the host framework are one-dimensional zigzag ladder chains (Fig. 1) made by edge-sharing of rings of four tetrahedral units (4-membered rings). Such chains propagate parallel to the crystallographic [110] and [1$\bar{1}$0] directions. [110]- and [1$\bar{1}$0]-chains alternate along the crystallographic c axis and are linked, spiro-like, *via* those tetrahedra that are centred by Zn(1) atoms. This results in the complete, with respect to fourfold connectivity interrupted, framework which generates, formally, a three-dimensional system of intersecting channels running along [110], [1$\bar{1}$0], [101] and [10$\bar{1}$] and being circumscribed by strongly elliptical 16-membered rings.

However, the channels are partly blocked by hydrogen bonds in $[H–O(P)]_4$ groupings (Fig. 1). Such a grouping, which is isolated within the three-dimensional framework, is illustrated in Fig. 2. The hydrogen-bonding system is considered below. First, we concentrate on the local situation around the centre, M, of such a grouping (Fig. 2c). M has site symmetry 222 (D_2) and is coordinated by four O(4) atoms at distances of 1.954 Å in a slightly distorted square-planar geometry (the four O(4)–M–O(4) angles within the plane range from 89.53 to 92.32°). Regarding the four next P atoms in the framework, the six P–M–P angles (ranging from 86.65 to 142.56°) come however somewhat closer to the tetrahedron angle of 109.5°. Allowing for some local distortions, the observed geometry indicates that the centres may be occupied by a number of metal cations (such as Ge^{4+}, Ti^{4+}, Si^{4+}), substituting for the four H atoms and leading to a fully four-connected framework of composition $[Zn_3M^{IV}(PO_4)_4]^{2-}$. In cases of tetravalent cations the framework charge will not be altered. Therefore, the structure of **I** may be favourably considered as a four-connected framework structure with local interruptions on one eighth of the four-connected sites. The four-connected network derived is of novel topology and considered more closely in the Discussion section.

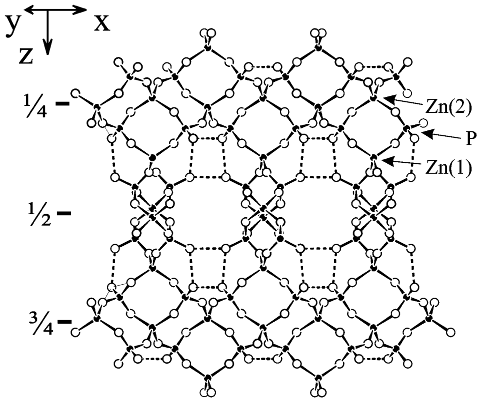

Fig. 1 Three-dimensional host framework of **I** as viewed down [110]. Zigzag ladder chains propagate along [110] at height z = ½ , and along [1$\bar{1}$0] at height z = ¼ and ¾. Hydrogen bonds are indicated by dotted lines. Black balls represent Zn and P atoms, white balls represent O atoms.

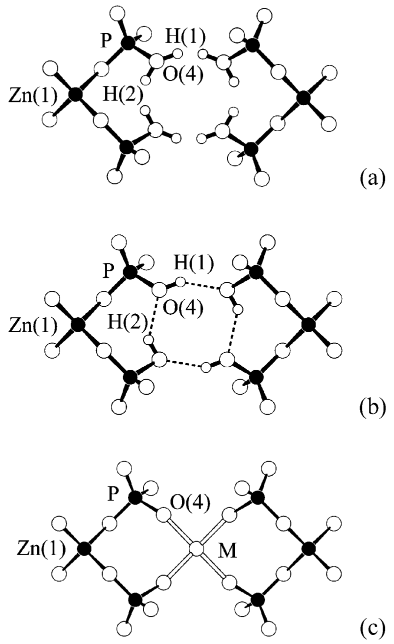

Fig. 2 $[H–O(P)]_4$ grouping of site symmetry 222 (D_2) in **I** as viewed down a local symmetry axis. (a) Statistical disorder of H atoms, (b) homodromic H-atom distribution, (c) connectivity of the centre M. Black balls represent Zn and P atoms, white balls represent O atoms.

Each H atom in a $[H–O(P)]_4$ grouping is disordered over two half-occupied positions, H(1) and H(2), and participates in two hydrogen bonds O(4)–H(1)···O(4a) and O(4)–H(2)···O(4b) (Fig. 2a). The donor–acceptor distances are 2.752 and 2.819 Å, and the angles at the H-atom positions are 147 and 134°. The existence of such hydrogen bonds is also in line with the IR spectrum which reveals a medium-strength, broad absorption band centred at 3373 cm^{-1} due to OH-stretching vibrations. The wavenumber is, according to well-known frequency-distance correlations,[9] in full accord with the donor–acceptor distances given above. Since tandem situations with two H atoms situated simultaneously between a pair of O atoms are unlikely,[10] an ordered, homodromic,[10] hydrogen-bonding system should exist in each grouping (Fig. 2b). Disorder is likely the result of the occurrence of both clockwise and counter-clockwise homodromic $[H–O(P)]_4$ systems in the crystal.

When the $[H–O(P)]_4$ groupings are taken into account, the sizes of the rings lining the three-dimensional channel system reduce from 16- to 8-membered (Fig. 1). As is shown in Fig. 3, the cavity that is generated at each channel intersection is topologically equivalent to the $[4^6 8^4]$ cavities found in the zeolite gismondine[11] (see Discussion). A cavity houses an ordered NMe_4^+ cation, the methyl C atoms of which possess large anisotropic displacement parameters, probably due to librational motion and only weak guest–host interactions. The shortest C···O and H···O guest–host distances are 3.188 and 2.48 Å, respectively.

Thermal behaviour

Variable-temperature powder XRD revealed that **I** remains crystalline up to 696 K, whereupon amorphization takes place. As is typical for the combustion of organic, a sharp weight loss of 18.6% is seen on the TG trace between 698 and 777 K (exothermic event). The weight loss comes close to the weight of the organic in **I** (calc. 20.1%). Three smaller, broad weight losses follow up to 1110 K. The total weight loss of 24.0 % agrees approximately with the release of organic and structural water (calc. 27.5%).

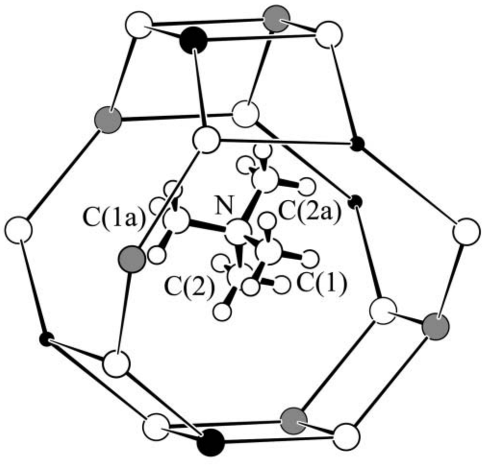

Fig. 3 $[4^6 8^4]$ cavity with guest cation in **I**. Large black balls represent Zn(1) centres, gray balls represent Zn(2) centres, white balls represent P centres, small black balls represent centres of $[H–O(P)]_4$ groupings, O atoms are omitted for clarity.

Discussion

The fully four-connected network obtained by replacing the four H atoms in each $[H–O(P)]_4$ grouping of **I** by a metal cation has topologically four different nodes which can be characterized by the coordination sequences[11] and long Schläfli symbols[11] listed in Table 3. To our knowledge, this net has not been reported before. Interestingly, the net is closely related to the net of the small-pore zeolite gismondine (GIS topology),[11] in that it possesses only 4- and 8-membered rings and generates a three-dimensional channel system with gismondine-type $[4^6 8^4]$ cavities at each channel intersection. In order to understand this relationship more deeply, it is best to consider first the relationship of the gismondine structure to the well-known diamond net, what has to our knowledge not yet been done in the literature. Therefore, we demonstrate in Fig. 4a that certain 4-membered rings (with their centres) correspond to the nodes and the remaining 4-membered rings to the links, respectively, of the diamond net and that, additionally, the centres of the $[4^6 8^4]$ cavities correspond to a second, complementary, diamond net interpenetrating the first one. In other words, zeolite gismondine is simply a periodic diamond-type array of $[4^6 8^4]$ cavities, and, in a terminology suggested recently,[12] an α-cristobalite structure. In this sense, the network derived from **I** may be considered as a novel periodic array of $[4^6 8^4]$ cavities, in which the centres of the cavities sit on the nodes of net #9 of O'Keeffe's compilation of uninodal four-connected nets (Figs 4b and 5b). Net #9, also a 6^6 net, is closely related to the diamond net (Fig. 5) and both nets can be readily intergrown.[13] Infinite double crankshaft chains,[14] a particular configuration of linear ladder chains on the bases of which the gismondine structure is frequently described (Fig. 6a), are not seen in the novel host network. Rather, "truncated' double crankshaft chains made of five 4-membered rings each occur (Fig. 6b). These finite units are linked together both spiro-like (at the M centres) and zigzag-like by sharing certain edges (around the

Table 3 Coordination sequences and long Schläfli symbols for the nodes (T_i) in the four-connected net derived from **I**

Node	Coordination sequence[a]	Long Schläfli symbol[a]
T_1 [Zn(1)]	4, 8, 16, 32, 48, 66, 96, 126, 152, 186	4.4.4.4.8.8
T_2 [Zn(2)]	4, 9, 18, 33, 50, 67, 92, 126, 156, 185	$4.4.4.8_2.8.8$
T_3 [M]	4, 10, 20, 32, 48, 72, 96, 118, 152, 196	$4.4.8.8.8_2.8_2$
T_4 [P]	4, 9, 18, 32, 49, 69, 94, 123, 154, 189	$4.4.4.8_2.8.8$

[a] See ref. 11.

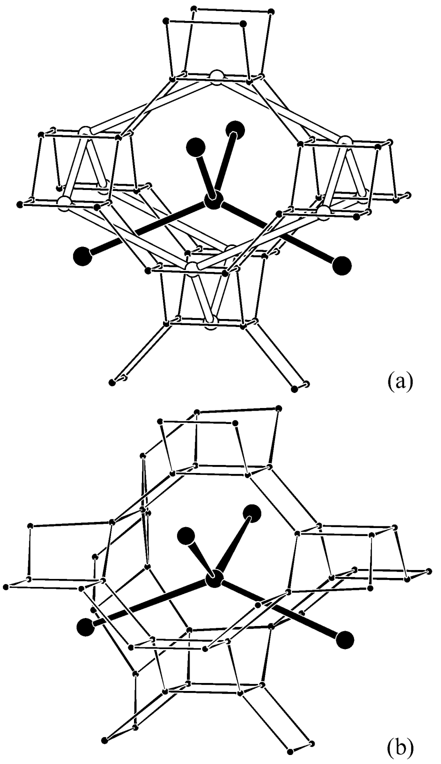

Fig. 4 (a) [$4^6 8^4$] cavity with surrounding 4-membered rings in zeolite gismondine. O atoms between the tetrahedral atoms are omitted for clarity. Large open balls and thick open lines indicate an adamantane-type unit cut out of the diamond net formed by certain 4-membered ring centres (see text). Large black balls and thick black lines indicate the diamond net of the cavity centres. (b) [$4^6 8^4$] cavity with surrounding 4-membered rings in **I**. Large black balls and thick black lines indicate net #9 of the cavity centres.

Zn(1) centres). The novel [$Zn_3M(PO_4)_4$](NMe_4)$_2$ host network has a framework density (FD)[11] of 14.0 T centres per 1000 Å^3.

The NMe_4^+ cation is well known to direct the formation of small cavities like the [$4^6 8^4$] cavities as found, for example, in aluminosilicate TMA-gismondine, [$AlSi_3O_8$](NMe_4)(H_2O).[15] Due to the mismatch between the low charge density of the relatively large organic cation and the high charge density in a zincophosphate with strictly alternating Zn- and P-centred tetrahedra and gismondine topology (0.5 negative charges per T atom), interruptions must occur in such a structure. It is however somewhat surprising that the outcome in the synthesis is an interrupted framework structure, **I**, with a more complex topology and not, as one might expect, with the simple gismondine topology. This topology is well known to be very flexible with regard to chemical composition and framework density.[11] We note that zinco-, cobalto- and beryllophosphates with non-interrupted gismondine structures and FD values (number of T centres per 1000 Å^3) between 15.0 and 19.2 have very recently been obtained in syntheses using diprotonated 1,2-diaminoethane and 1,3-diaminopropane as templates.[2a,16]

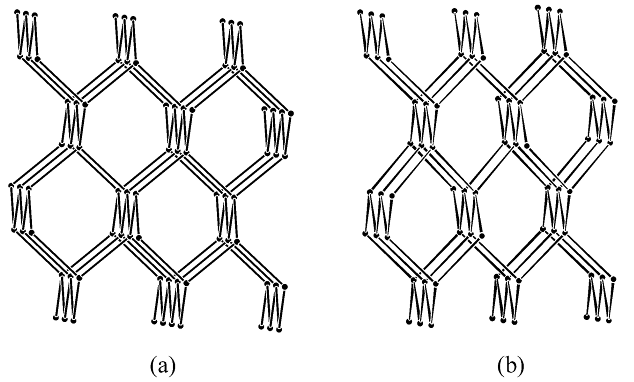

Fig. 5 (a) Diamond net of [$4^6 8^4$] cavity centres in gismondine. (b) Net #9 of [$4^6 8^4$] cavity centres in **I**. The nets represent the different three-dimensional intersecting channel systems existing in gismondine and **I**.

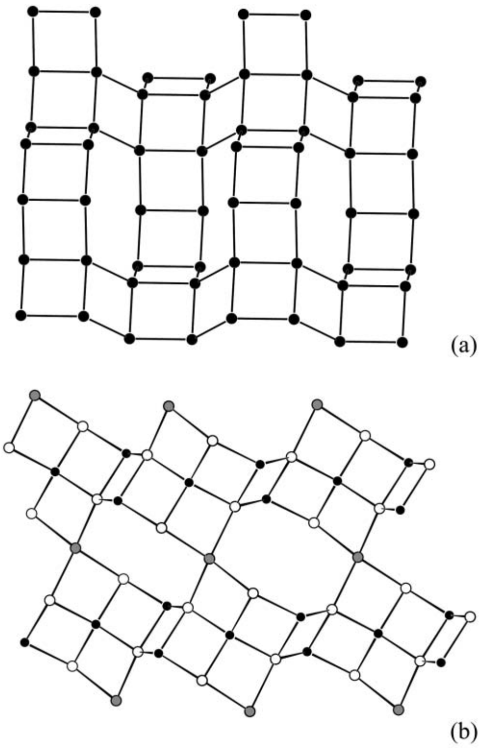

Fig. 6 (a) Linkage of 4-membered rings in gismondine; double crankshaft chains run in horizontal and vertical directions. (b) Linkage of 4-membered rings in **I**; "truncated' double crankshaft chains run from top left to bottom right; white balls represent P centres, black balls represent Zn centres, gray balls represent centres of [H–O(P)]$_4$ groupings.

A related case is a zincophosphate, [$Zn_2(PO_4)(H_{1.5}PO_4)_2$]-($C_4H_{12}N_2$), with the simple sodalite (SOD) topology templated by diprotonated piperazine molecules.[17] In this compound one sixth of the tetrahedral framework sites are local interruptions similar to those found in **I**, yet being more distorted and having only three H atoms distributed in one very strong and two normal hydrogen bonds.[3a] Interestingly, in accord with charge-density matching and template shape, a piperazinium gallium(III)–cobalt(II) phosphate, [$GaCo_2(PO_4)_3$]($C_4H_{12}N_2$), with a fully four-connected sodalite structure has been also prepared.[18] Also, well-known are the local 4(H^+) for Si^{4+} substitutions occurring in the tetrahedral sites ($SiO_4 = H_4O_4$) of natural and synthetic garnets.[19]

Taking all together, it appears interesting to investigate whether tetravalent cations (such as Si^{4+}, Ge^{4+}, Ti^{4+}) can be combined with Zn^{2+} (or other divalent cations) and P^{5+} into novel open-framework oxide materials with known or new structures and useful properties. Such experiments have been started.

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