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$Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$: An interrupted-framework zincogermanate built from $[GeO_3(OH)]$ and $[Ge_2(OH)_2]$ units†

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A new layered germanate, $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$, has been synthesized from an aqueous solution containing germanium dioxide, zinc acetate and sodium hydroxide. Room temperature single crystal X-ray diffraction data indicate an orthorhombic cell with $a = 13.036(3)$ Å, $b = 8.7286(17)$ Å, $c = 12.938(3)$ Å, space group *Pbcn* (no. 60), and $Z = 4$. Chains of orthogonal four-rings, consisting of corner-sharing $[Ge_2Zn_2]$ units bridged at the zinc centers, are connected to form a new tetrahedral sheet structure containing bifurcated 10-membered rings and the unique building blocks, $[GeO_n(OH)_{4-n}]$ ($n = 1, 2$). The zincogermanate sheets are stacked along the *c*-axis and connected both by Na–O electrostatic interactions and a hydrogen bonding network composed of bound water molecules and terminal hydroxide anions.

Introduction

Interest in the synthesis of new microporous crystalline inorganic oxides has been stimulated by their extensive use in commercial applications such as catalysis, ion-exchange, and separation technologies.[1,2] These materials are based upon framework structures composed of corner-sharing tetrahedral $[TO_4]$ units (T = tetrahedrally coordinated cation) that form open ring structures. Since the properties of these materials are intimately tied to their chemical composition and structure, the synthesis of new microporous inorganic oxides with new framework structures and compositions is of fundamental importance.

Our laboratory is interested in the synthesis and properties of highly-charged germanate frameworks incorporating lithium and zinc because these elements are non-toxic and favor small T–O–T angles that are necessary for the formation of small rings, that in turn, can result in low framework densities. There are only a limited number of zincogermanates known and with the exception of a melilite-type compound,[3] all are condensed phases.[4–7] In the course of this work, we have synthesized a highly-crystalline interrupted framework zincogermanate, $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$. It crystallizes with a previously unobserved layer topology and is one of the few known layered germanates.[3,8,9] The layers are constructed from chains of 4-membered rings containing $[GeO_3(OH)]$, $[GeO_2(OH)_2]$, and $[ZnO_4]$ tetrahedral units that condense to form bifurcated 10-member rings. In this paper we report the synthesis and structure of this zincogermanate.

Experimental

Synthesis

Crystals of $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$ were obtained using hydrothermal techniques. A suspension was prepared by adding 0.114 g $Zn(CH_3COO)_2\cdot 2H_2O$ (0.519 mmol) and 0.984 g GeO_2 (9.41 mmol) sequentially to 4.44 g of 10 M NaOH (1.03 mmol NaOH) in a polymethylpentene (PMP) ehrlenmeyer flask over the course of an hour. While all of the zinc acetate dissolved in the alkaline solution, approximately half of the GeO_2 was dispersed throughout as a fine white powder. To this, 7.98 g of a solution with a mass fraction of 40% dimethylamine with 70.9 mmol DMA in H_2O was added. To obtain crystals suitable for diffraction studies, the mixture was heated at 60 °C for 7 d in a sealed PMP flask to produce a viscous liquid with a fine white solid dispersed throughout. The mixture was heated at 110 °C for 6 months in a Teflon pouch that was contained within a hermetically sealed stainless steel bomb. After cooling to room temperature, the product was recovered by filtration and dried. Before washing, the mother liquor smelled distinctly of ammonia. The resultant crystals were colorless and tabular in habit and ranged in size from 0.02 mm to 0.2 mm (longest dimension). Crystals can be grown in shorter times by heating the above reaction mixture for 14 days at temperatures ranging between 110 °C to 150 °C. Tabular crystals produced in these reactions are as large as 2 mm × 1 mm, but are intergrown and twinned and therefore not of sufficient quality for single crystal analysis.

Single crystal X-ray diffraction

A suitable crystal (0.2 mm × 0.1 mm × 0.02 mm) was carefully selected under a polarizing microscope and glued to a thin glass fiber with epoxy resin. Data were collected on a Bruker Smart-CCD diffractometer equipped with a normal-focus X-ray-tube (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. A total of 1660 frames were collected at room temperature with a combination of ϕ and ω scans in the 2θ

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†Electronic supplementary information (ESI) available: layered structure; zigzag network of octahedrally coordinated nations; coordination environments of Na(1), Na(2) and Na(3). See http://www.rsc.org/suppdata/jm/b0/b004668j/

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Table 1 Crystallographic data collection and refinement parameters for $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot2H_2O$

	$Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot2H_2O$
Empirical formula	H_4 O_8 Ge_2 Na_2 Zn
FW	388.62
Crystal system	Orthorhombic
a/Å	13.036(3)
b/Å	8.728(2)
c/Å	12.938(3)
V/Å^3	1472.2(5)
T/K	293(2)
Space group	*Pbcn* (no. 60)
Z	4
μ/mm^{-1}	9.370
Measured/independent reflections/R_{int}	9377/1712/0.0602
Data/parameters ratio	12.4
R^a (all data)	0.0595
$R_w{}^b$ (all data)	0.1293
Goodness-of-fit on F^2	1.060

$^aR=\Sigma(|F_{\text{obs}}|-|F_{\text{calc}}|)/\Sigma|F_{\text{obs}}|$. $^bR_w=\{\Sigma[w(F^2_{\text{obs}}-F^2_{\text{calc}})^2]/\Sigma[w(F^2_{\text{obs}})^2]\}^{0.5}$.

region 6.26° to 56.50°. Scan widths of $\Delta\phi$ and $\Delta\omega$ were 0.30° and exposure times were 20 s per frame. Unit cell parameters were obtained by a global refinement of the positions of all reflections, as performed by the processing program SAINT.[10] Systematic absences uniquely identified the space group *Pbcn*. An absorption correction was applied using SADABS.[10] The structure was solved by direct methods followed by successive Fourier difference syntheses, with all calculations performed using SHELXTL.[11] Final full-matrix refinements were against F^2. Anisotropic displacement factors were included for all the atoms except hydrogen. All hydrogen atom parameters were refined. Relevant crystallographic parameters are summarized in Table 1. Atomic positions and displacement parameters are listed in Table 2. Derived interatomic distances and angles are found in Table 3 and Table 4. CCDC reference number 1145/246. See http://www.rsc.org/suppdata/jm/b0/b004668j/ for crystallographic files in .cif format.

Bulk sample analysis

Samples were initially examined by powder X-ray diffraction to establish phase identity and purity, using a Scintag PAD-X diffractometer. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50. Data were collected on small single crystals under a N_2 atmosphere with a heating rate of 10 °C min^{-1} to 800 °C. Powder X-ray diffraction data were used to identify the decomposition product.

Results and discussion

The basis of this structure is an infinite linear chain that consists of orthogonally oriented corner-sharing $[Ge_2Zn_2]$ 4-rings (Fig. 1) that run along [010]. This building unit is identical to the $[Al_2P_2O_8]_\infty$ chains that are the building blocks of aluminophosphates.[12] Condensation of these chains occurs between $[Ge(2)O_3(OH)]$ tetrahedra to form layers consisting of bifurcated 10-member rings (Fig. 2). The layers are corrugated and are nested together; $[Ge(1)O_2(OH)_2]$ tetrahedra on adjacent layers point towards each other to form an interpenetrating layer surface (Fig. 3). The resulting framework contains small pores with approximate diameter of 5.0 Å × 7.5 Å, as measured from the center of the oxygen atoms. The rings in $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot2H_2O$ contain water and charge-balancing sodium cations that hold the layers together through electrostatic interactions.

Zinc coordination distances are regular with an average Zn–O bond length of 1.95 Å while in the $GeO_2(OH)_2$ and $GeO_3(OH)$ tetrahedra, the Ge–OH bonds are longer than the Ge–O bonds, as expected (Table 3). In the 4-ring, the average O–T–O angles of 119.0° deviate significantly from their expected values of 109.5° to relieve torsional strain in the 4-ring sub-unit (Table 4). Sodium cations found throughout the pore structure link the sheets. Na(2) is located between two layers and is coordinated by three framework oxygen atoms from adjacent layers. Na(1) and Na(3) are coordinated by the oxygen of the bound water and 5 framework oxygens. Na(1) is coordinated by three oxygens from two adjacent layers. Na(3) interacts with three layers; it is bound to four oxygens from a single layer and one oxygen from each adjacent layer.

H–O···H bonding plays an important role in linking the layers. The terminal hydroxyl groups are directed towards adjacent layers and form hydrogen bonds (≈1.8 Å) with oxygen on opposing sheets. The bound water forms HO···H bonds on the order of 1.6 Å, although hydrogen is bound to two framework oxygens in the 10-ring of a single layer.

Bond valence sum calculations were performed to check the validity of this model through the computation of the total valence at each site.[13] For the metal cations, calculated results are in excellent agreement with expected values: Ge(1) = 3.93(8), Ge(2) = 3.95(7), Zn = 2.04(5), Na(1) = 1.05(2), Na(2) = 1.02(2), Na(3) = 1.07(3). Hydrogen and oxygen had reasonable bond

Table 2 Final refined coordinates (Å), anisotropic displacement parameters and equivalent isotropic displacement parameters (A^3) for $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot2H_2O$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	$U_{\text{eq}}{}^a/U_{\text{iso}}$
Ge(1)	8d	0.3776(1)	0.1260(1)	0.5009(1)	0.011(1)	0.007(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.009
Ge(2)	8d	0.1204(1)	−0.1179(1)	0.2513(1)	0.009(1)	0.006(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.010
Zn(1)	8d	0.2510(1)	0.1244(1)	0.1269(1)	0.011(1)	0.009(1)	0.010(1)	0.000(1)	0.000(1)	0.000(1)	0.010
Na(1)	8d	0.1491(2)	0.2569(2)	0.3749(2)	0.017(1)	0.013(1)	0.019(1)	−0.002(1)	−0.001(1)	0.000(1)	0.016
Na(2)	4a	0	0	0.5	0.022(2)	0.016(2)	0.021(2)	0.000(1)	0.005(2)	0.003(2)	0.020
Na(3)	4c	0	0.5104(4)	0.25	0.021(2)	0.014(2)	0.022(2)	0	−0.009(2)	0	0.019
O(1)	8d	0.1312(3)	−0.0203(5)	0.3729(3)	0.015(2)	0.009(2)	0.015(2)	−0.001(2)	−0.001(2)	−0.003(2)	0.013
O(2)	8d	0.3690(3)	0.0298(5)	0.3792(3)	0.016(2)	0.011(2)	0.013(2)	−0.001(2)	0.000(2)	−0.001(2)	0.013
O(3)	8d	0.4992(3)	0.2199(5)	0.5006(3)	0.008(2)	0.012(2)	0.017(2)	0.005(2)	−0.001(2)	−0.003(2)	0.015
O(4)	8d	0.1213(3)	0.0188(4)	0.1555(3)	0.011(2)	0.014(2)	0.018(2)	−0.001(1)	0.000(2)	−0.002(2)	0.015
O(5)	4c	0	−0.2119(6)	0.25	0.006(3)	0.011(3)	0.022(3)	0	0.002(3)	0	0.013
O(6)	8d	0.3764(4)	−0.0094(4)	0.5977(3)	0.012(2)	0.011(2)	0.018(2)	0.005(2)	−0.001(2)	−0.001(2)	0.013
O(7)	8d	0.2830(3)	0.2647(4)	0.5010(3)	0.014(2)	0.010(2)	0.011(2)	−0.001(2)	−0.001(2)	0.005(2)	0.012
O(8)	8d	0.2857(3)	0.2422(4)	0.2502(3)	0.011(2)	0.008(2)	0.014(2)	−0.001(2)	−0.001(2)	−0.004(2)	0.011
O(9)	4d	0	0.2392(7)	0.25	0.016(3)	0.014(3)	0.021(3)	0	0.002(3)	0	0.017
H(1)	8d	0.167(7)	−0.086(8)	0.420(6)							0.04(2)
H(2)	8d	0.329(7)	0.091(8)	0.336(7)							0.04(3)
H(3)	8d	0.542(6)	0.143(7)	0.462(6)							0.03(2)
H(9)	8d	0.044(7)	0.133(7)	0.218(7)							0.05(3)

$^aU_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected derived interatomic distances (Å) for $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$

Ge(1)–O(6)	1.722(4)	Ge(2)–O(4)	1.721(4)
Ge(1)–O(7)	1.728(4)	Ge(2)–O(8)	1.728(3)
Ge(1)–O(3)	1.785(4)	Ge(2)–O(5)	1.772(3)
Ge(1)–O(2)	1.788(4)	Ge(2)–O(1)	1.795(4)
<Ge(1)–O>	1.76(2)	<Ge(2)–O>	1.75(2)
Zn(1)–O(7)	1.946(4)	Zn(1)–O(8)	1.951(4)
Zn(1)–O(6)	1.955(4)	Zn(1)–O(4)	1.960(4)
		<Zn(1)–O>	1.953(3)
Na(1)–O(7)	2.390(5)	Na(1)–O(2)	2.395(5)
Na(1)–O(8)	2.407(5)	Na(1)–O(1)	2.430(5)
Na(1)–O(9)	2.533(3)	Na(1)–O(3)	2.541(5)
Na(2)–O(1)	2.379(4) 2 ×	Na(2)–O(3)	2.445(5) 2 ×
Na(2)–O(4)	2.565(4) 2 ×	Na(3)–O(2)	2.396(4) 2 ×
Na(3)–O(5)	2.424(6)	Na(3)–O(6)	2.545(4) 2 ×
Na(3)–O(9)	2.367(8)		
O(1)–H(1)	0.96(8)	O(3)–H(3)	1.01(8)
O(2)–H(2)	0.93(9)	O(9)–H(9)	1.17(7)
H(1) O(7)	1.79(8)	O(1)–H(1)···O(7)	2.742(6)
H(2)···O(8)	1.81(8)	O(2)–H(2)···O(8)	2.721(6)
H(3)···O(6)	1.77(8)	O(3)–H(3)···O(6)	2.762(6)
H(9)···O(4)	1.61(8)	O(9)–H(9)···O(4)	2.774(6)

Table 4 Selected derived interatomic angles (°) for $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$

O(6)–Ge(1)–O(7)	118.3(2)	O(6)–Ge(1)–O(3)	109.0(2)
O(7)–Ge(1)–O(3)	108.1(2)	O(6)–Ge(1)–O(2)	108.5(2)
O(7)–Ge(1)–O(2)	106.5(2)	O(3)–Ge(1)–O(2)	105.6(2)
O(4)–Ge(2)–O(8)	118.6(2)	O(4)–Ge(2)–O(5)	108.6(2)
O(8)–Ge(2)–O(5)	107.4(2)	O(4)–Ge(2)–O(1)	107.5(2)
O(8)–Ge(2)–O(1)	106.7(2)	O(5)–Ge(2)–O(1)	107.3(2)
O(7)–Zn(1)–O(8)	118.3(2)	O(7)–Zn(1)–O(6)	106.5(2)
O(8)–Zn(1)–O(6)	103.5(2)	O(7)–Zn(1)–O(4)	101.2(2)
O(8)–Zn(1)–O(4)	107.0(2)	O(6)–Zn(1)–O(4)	121.0(2)
Ge(2)–O(4)–Zn(1)	117.9(2)	Ge(1)–O(6)–Zn(1)	120.0(2)
Ge(1)–O(7)–Zn(1)	120.8(2)	Ge(2)–O(8)–Zn(1)	122.9(2)
Ge(2)–O(5)–Ge(2)	124.8(3)		
Ge(2)–O(1)–H(1)	108(5)	O(1)–H(1)–O(7)	169(5)
Ge(1)–O(2)–H(2)	108(5)	O(2)–H(2)–O(8)	164(5)
Ge(1)–O(3)–H(3)	101(4)	O(3)–H(3)–O(6)	176(5)
H(9)–O(9)–H(9)	84(5)	O(9)–H(9)–O(4)	164(5)

valence sums when the errors in H^+ were taken into consideration. These errors result from the difficulty in accurately determining the position of hydrogen using X-rays.

Amines or alkali-metal cations are added as structure-directing agents to influence the structural connectivity, size and shape of pores in open-framework materials. Some framework structures can be formed only in the presence of a single structure-directing agent while others can be synthesized from many.[14] The roles of DMA and alkali metal hydroxides were studied in an effort to understand their role in product formation.

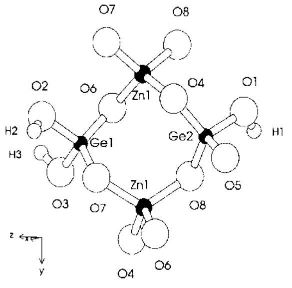

Fig. 1 $[Ge_2Zn_2]$ 4-rings form the basis of the chains from which the layer structure is built. Each germanium is both chemically and crystallographically unique.

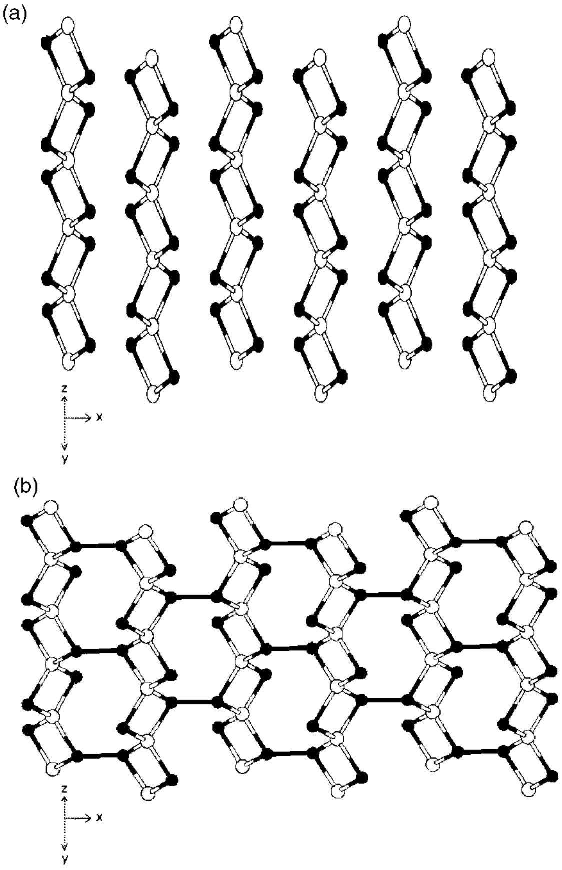

Fig. 2 (a) $[Ge_2Zn_2]$ chains are linked by oxygen atoms through Ge(2) to form (b) bifurcated 10-member rings that make up the layers of $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$. The bridging oxygen atoms are omitted for clarity. Projected along the crystallographic [011] direction. Tetrahedral nodes: $[ZnO_4]$ – unshaded, $[GeO_x(OH)_{4-x}]$ – shaded.

While the presence of amine does not appear to influence the identity of the product, it affects both purity and crystal quality. The highest yields are obtained using the short synthesis described in the Experimental section. $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$ can also be synthesized from mixtures containing no amine. These reactions give similar yields of approximately 70%, but the product is a mass of small, intergrown crystals with poorly defined edges. In reactions without DMA, an unidentified crystalline impurity phase is observed with peaks at 6.98 Å, 5.55 Å, 4.24 Å, 3.54 Å, 3.10 Å,

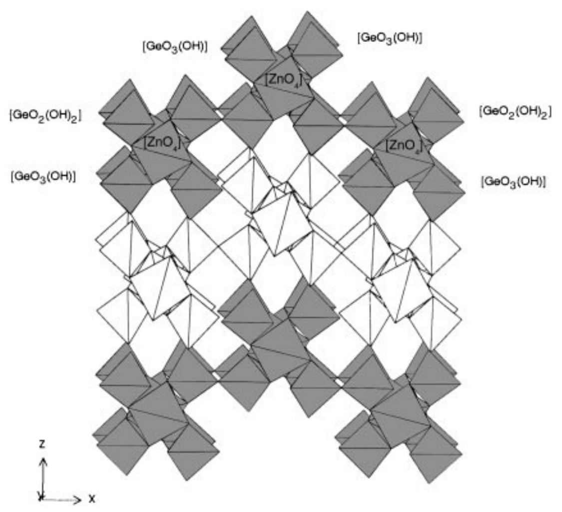

Fig. 3 The layers of $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$ are corrugated and stack together. Individual layers are shaded. Projected slightly off the crystallographic [010] direction.

2.70 Å, and 2.25 Å. Close inspection of X-ray powder diffraction data collected for longer times from syntheses using DMA reveals the presence of the impurity phase as a very minor component. These results suggest two possible roles for the amine in these reactions: stabilizing solvated germanium and/or zinc to facilitate the growth of large crystals and suppressing the formation of impurity phases.

The identity of the alkali metal cation employed has a much greater influence on the reaction outcome. While reactions with NaOH invariably gave crystals, solutions containing KOH, RbOH and CsOH produced white solids that were X-ray amorphous; no solid products could be recovered from reactions with LiOH. There is extensive hydrogen bonding that stabilizes the structure of $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$. For this structure to form, the charge-balancing cation must not disrupt the network of hydrogen bonding. A large charge-balancing cation such as K^+ ($r_{K-O} = 2.74$ Å *vs.* $r_{Na-O} = 2.38$ Å)[15] would destroy these interactions. Although Li^+ would strengthen interlayer interactions, it would destabilize the hydrogen bonding within the $[Ge_2Zn_2]$ chains. This suggests that hydrogen bonding plays a role in the structure formation of this material.

Thermal analysis data are also consistent with extensive hydrogen bonding. The weight loss from the condensation of hydroxyl groups and bound water is calculated to be 9.27%. The TGA study reveals a single weight loss of 9.2% between 250 °C and 300 °C and results in framework collapse to a denser phase, Na_2ZnGeO_6 (ICDD-JCPDS:[16] 37-0257). Although dehydration and decomposition of framework materials often occur at different temperatures, it is not surprising that both events happen in a single step because of the extensive hydrogen bonding throughout this phase.

Because of the layered structure of $Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$, ion-exchange of the charge-balancing cations is possible even though direct synthesis of other alkali metal analogs is not. Initial attempts to exchange Li^+ for Na^+ using 2.0 M $LiNO_3$(aq) at room temperature indicate that a topotactic reaction occurs. Efforts are being made to identify the product and a more detailed investigation of the ion-exchange properties are planned.

Conclusions

$Na_8[Zn_4Ge_8O_{18}(OH)_{12}]\cdot 2H_2O$, a new hydrated sodium zincogermanate has been prepared by hydrothermal methods. It exhibits a new tetrahedral sheet structure composed of condensed chains with stoichiometry $[Ge_2Zn_2]$ that form 4-rings and bifurcated 10-rings. It is one of a limited number of zincogermanate frameworks. The structural integrity of the title compound is maintained both through electrostatic interactions and hydrogen bonding, providing another example illustrating the role that hydrogen bonding plays in structure formation. Preliminary results indicate that the compound exhibits ion-exchange chemistry.

Acknowledgements

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