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Layered Structures Constructed from New Linkages of $Ge_7(O,OH,F)_{19}$ Clusters

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Three new germanate solids, ASU-19, ASU-20-DAPe, and ASU-20-DACH, have been synthesized under hydrothermal conditions using respectively 1,4-diaminobutane (DAB), 1,5-diaminopentane (DAPe), and 1,4-diaminocyclohexane (DACH) as bases. The structures of ASU-19 and ASU-20-DACH have been characterized by single-crystal X-ray diffraction: ASU-19, $Ge_{14}O_{29}X_4{\cdot}[GeOX_2]{\cdot}[H_2DAB]_3{\cdot}3.8H_2O$ ($X = F$ or OH), space group $P\bar{1}$, $a = 11.4191(5)$, $b = 12.0525(6)$, $c = 18.1847(8)$ Å, $\alpha = 90.704(1)°$, $\beta = 92.635(1)°$, $\gamma = 91.389(1)°$, $V = 2499.1(2)$ Å^3; ASU-20-DACH: $Ge_7O_{14}X_3{\cdot}[H_2DACH]_{1.5}{\cdot}2H_2O$, space group $C2/c$, $a = 15.9525(11)$, $b = 17.5476(12)$, $c = 19.0027(13)$ Å, $\beta = 109.446(1)°$, and $V = 5015.9(6)$ Å^3. The structure of ASU-20-DAPe, $Ge_7O_{14}X_3{\cdot}[H_2DAPe]_{1.5}{\cdot}H_2O$, has been determined from X-ray powder diffraction data: space group $C2/c$, $a = 16.3180(5)$, $b = 16.6125(4)$, $c = 17.8898(6)$ Å, $\beta = 99.684(2)°$, $V = 4780.5(3)$ Å^3. All three structures are based on the assembly of the same cluster $Ge_7(O,OH,F)_{19}$. The two ASU-20 structures consist of a slab of four-connected clusters. In ASU-19, the same layers are connected pairwise through a GeO_2X_2 spacer, generating a slab structure, with slab thickness ca. 20 Å. The existence of the same layer in the presence of three different organic bases shows the adaptability of the structures to molecules differing in size, shape, and symmetry.

Introduction

The synthesis of oxide frameworks with ever-increasing pore size and decreasing density is currently an active and intensely challenging field. Particular interest is associated with frameworks constructed from polyatomic structure building units (SBUs) containing metal atoms in mixed 4-, 5-, and 6-coordination and anions in 1-, 2-, and 3-coordination (compare conventional zeolite frameworks with cations in 4-coordination and anions in 2-coordination). The main classes of materials are (a) phosphates, particularly of aluminum and gallium,[1,2] and (b) germanates;[3−7] among these materials are those with the largest ring (24-ring) size[2,5,6] and the lowest framework density (8.6 Ge nm^{-3})[5] found to date.

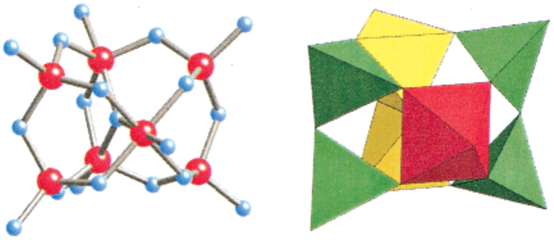

Figure 1. $Ge_7(O,OH,F)_{19}$ cluster. Left, as a ball-and-stick model (Ge, red). Right, as Ge-centered polyhedra; tetrahedra, green; trigonal bipyramids, yellow; and octahedron, red.

Evidence, especially from NMR studies of phosphates,[8] is now accumulating that the SBUs, or at least closely related precursors (PNBUs), have reality beyond being a mere conceptual geometrical unit, and this is reinforced by the occurrence of one SBU in a number of related structures.[1] One such SBU (Figure 1), $Ge_7(O,OH,F)_{19}$, has been previously noted as a robust unit and used to produce the 3-D germanates ASU-12[4] and ASU-16.[5] The same SBU has recently been found linked by isolated tetrahedra in a germanate with framework composition $Ge_{10}O_{21}(OH)$.[7] Here we describe the preparation and characterization of two single-layer ger-

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manates (ASU-20-DACH and ASU-20-DAPe) composed of $Ge_7(O,OH,F)_{19}$ units linked in a new way to produce 4-coordinated layers. We also describe ASU-19 in which the same layers are found but now further linked by single tetrahedra into double-layer slabs.

Experimental Section

Synthesis. ASU-19 was prepared under hydrothermal conditions from a mixture of germanium dioxide, water, 1,4-diaminobutane (DAB, 99%, Aldrich), pyridine, and hydrofluoric acid (48 wt %) with a typical molar ratio of 1:80:12:40:6 GeO_2:H_2O:DAB:pyridine:HF. A 23-mL Teflon-lined vessel was filled with ca. 3 mL of mixture and heated at 160 °C for 4 days. On the basis of crystal structure and elemental analysis the material was formulated as $Ge_{14}O_{29}X_4\cdot[GeOX_2]\cdot[H_2DAB]_3\cdot 3.8H_2O$. Anal. Calcd: C 7.25, H 2.28, N 4.22, Ge 54.01, F 3.8. Found: C 7.44, H 2.35, N 4.22, Ge 53.25, F 2.7. Note that quantitative analysis for F may be less reliable in materials of this kind.

ASU-20-DAPe was prepared under the same conditions as ASU-19, using 1,5-diaminopentane (DAPe, 95%, Aldrich) as a base. The molar ratio is 1:70:14:40:3 GeO_2:H_2O:DAPe:pyridine:HF. The mixture was heated at 140 °C for 4 days. On the basis of the crystal structure with unambiguously resolved atoms (other than distinguishing F and OH), the material was formulated as $Ge_7O_{14}X_3\cdot[H_2DAPe]_{1.5}\cdot H_2O$.

ASU-20-DACH was obtained from a mixture heated for 6 days at 180 °C, with composition 1:110:6:40:3 GeO_2:H_2O:DACH:pyridine:HF, where the DACH stands for *trans*-1,4-diaminocyclohexane (Aldrich). On the basis of the crystal structure the material was formulated as $Ge_7O_{14}X_3\cdot[H_2DACH]_{1.5}\cdot 2H_2O$.

The resulting products were washed with water and dried in air at room temperature. ASU-19 and ASU-20-DACH consist of crystals with platelike morphology suitable for single-crystal analysis; a white powder is obtained in the case of ASU-20-DAPe.

Structure Determination. Colorless crystals of ASU-19 (dimensions 0.21 × 0.18 × 0.05 mm^3) and ASU-20-DACH (dimensions 0.25 × 0.20 × 0.05 mm^3) were selected for single-crystal analysis at room temperature. Intensities were collected using a Bruker Smart-CCD area detector with Mo Kα radiation. Absorption corrections were performed using the SADABS program.[9] The Siemens/Bruker program SHELXTL-PC software package was utilized to solve the structures by direct methods. The refinements were performed against all F^2 with anisotropic thermal parameters for all non-hydrogen atoms.

X-ray powder diffraction data for ASU-20-DAPe were collected on a Siemens D-5000, equipped with a graphite monochromator, using Cu Kα radiation, over the range 7−80° (2θ). The powder pattern was indexed in the monoclinic crystal system. The evaluation of the systematic absences led to the space groups *Cc* and *C*2/*c*. The structure was solved by direct methods in the space group *C*2/*c* using EXPO.[10] Completion of the structure by Fourier difference and Rietveld refinement were performed using the GSAS software package.[11] Soft constraints were applied on distances Ge−O, C−C, and C−N throughout all the refinement. The final Rietveld refinement is shown in Figure 2.

The crystal data for the three compounds are reported in Table 1. The atomic coordinates and selected bond distances and angles are available as supporting information.

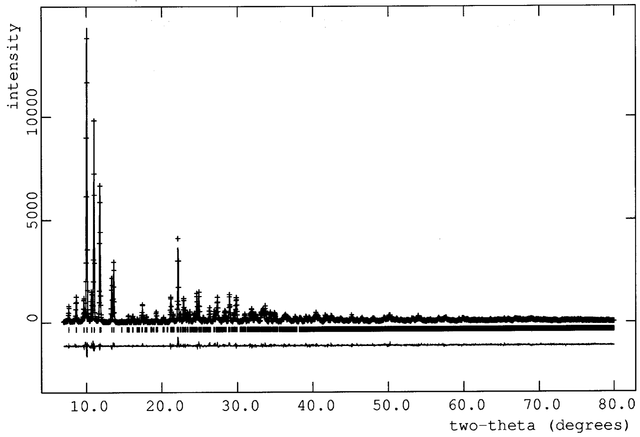

Figure 2. Observed and calculated powder X-ray diffraction pattern of DAPe-ASU-20.

Results and Discussion

The structures of ASU-19 and ASU-20 are made of a cluster $Ge_7(O,OH,F)_{19}$, which consists of one octahedral, two trigonal prismatic, and four tetrahedral Ge atoms with one 3-coordinated anion at its center (Figure 1). Seven of the anions are singly coordinated and available for linkage when the clusters condense into a framework. The same cluster is observed in ASU-12[4] and ASU-16,[5] which are prepared under similar conditions using dimethylamine and 1,4-diaminobutane as bases, respectively. In ASU-12 and ASU-16 the clusters are five-connected and the framework composition is formulated $Ge_7O_{12}O_{5/2}X_2{}^{3-}$, where singly coordinated anions are formulated as X standing for either F or OH as they are difficult to discriminate by X-ray analysis, and elemental analysis for F is less reliable in materials of this type. In ASU-20 each cluster is connected to its neighbors in the same way (see below) but with a different overall network topology. In ASU-19 the same heptamer has new modes of linkage to five neighbors (Figure 3); one of which is a single GeO_4 tetrahedron rather than a cluster.

In discussing germanate frameworks of this sort (with organic bases as counterions) it is useful to make the following general observations. (a) The valence of Ge is 4. (b) Singly coordinated anions are X = F or OH. (Contrast the situation in phosphates where P=O double bonds to singly coordinated O are common.) (c) Multiply bonded atoms are O. As a consequence of these "rules" we can calculate the charge per cluster from the geometry. If there are g_5 5-coordinated Ge atoms, g_6 6-coordinated Ge atoms, and x_3 3-coordinated anions, the charge per cluster is $z = x_3 - g_5 - 2g_6$. In particular for structures based on $Ge_7(O,OH,F)_{19}$ clusters ($x_3 = 1$, $g_5 = 2$, $g_6 = 1$), with or without additional tetrahedral Ge atoms, the charge per cluster is always −3. This is borne out in the structure analysis of ASU-19 and ASU-20 which clearly shows the presence of 3/2 dibasic units per germanate cluster.

In ASU-12 and ASU-16 the clusters are linked into 3-connected plane nets, 6^3 and 4.8^2 respectively, that are then linked to the nets above and below to make a 5-connected framework. In ASU-19 the layers are 4-connected 4^4 nets that are connected in pairs by a fifth link to produce a slab structure (Figure 3) with overall thickness ca. 20 Å. In the *ab* plane, the layer of clusters

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Table 1. Crystallographic Data for ASU-19, ASU-20-DACH, and ASU-20-DAPe

compound	ASU-19	ASU-20-DACH	ASU-20-DAPe
chemical formula	$Ge_{14}O_{29}F_4 \cdot [GeO(OH)_2] \cdot [H_2DAB]_3 \cdot 3.8H_2O$	$Ge_7O_{14}F_3 \cdot [H_2DACH]_{1.5} \cdot 2H_2O$	$Ge_7O_{14}F_3 \cdot [H_2DAPe]_{1.5} \cdot H_2O$
crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$	monoclinic, $C2/c$
cell parameters (Å,°)	$a = 11.4191(5)$, $\alpha = 90.704(1)$ $b = 12.0525(6)$, $\beta = 92.635(1)$ $c = 18.1847(8)$, $\gamma = 91.389(1)$	$a = 15.9525(11)$ $b = 17.5476(12)$, $\beta = 109.446(1)$ $c = 19.0027(13)$	$a = 16.3180(5)$ $b = 16.6125(4)$, $\beta = 99.684(2)$ $c = 17.8898(6)$
cell volume (Å^3)	$V = 2499.1(2)$	$V = 5015.9(6)$	$V = 4780.5(3)$
Z	2	8	8
wavelength (Å)	$\lambda = 0.71073$	$\lambda = 0.71073$	$\lambda = 1.54056$
contributing reflections	20461 measured, 8833 independent	24474 measured, 5778 independent	1586
independent atoms	80	39	37
$R1$, $wR2$[a]	$R1 = 4.73\%$, $wR2 = 8.63\%$	$R1 = 5.00\%$, $wR2 = 10.45\%$	–
R_{wp}, R_B[b]	–	–	$R_{wp} = 10.2\%$, $R_B = 4.6\%$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/w(F_o)^2]^{1/2}$ for 6946 reflections satisfying $I > 2\sigma(I)$ in the case of ASU-19 and for 4991 reflections satisfying $I > 2\sigma(I)$ in the case of ASU-20-DACH. [b] $R_{wp} = [\Sigma w_I(y_{io} - y_{ic})^2/\Sigma w_i y_{io}^2]^{1/2}$; $R_B = \Sigma|I_o - I_c|/\Sigma I_o$.

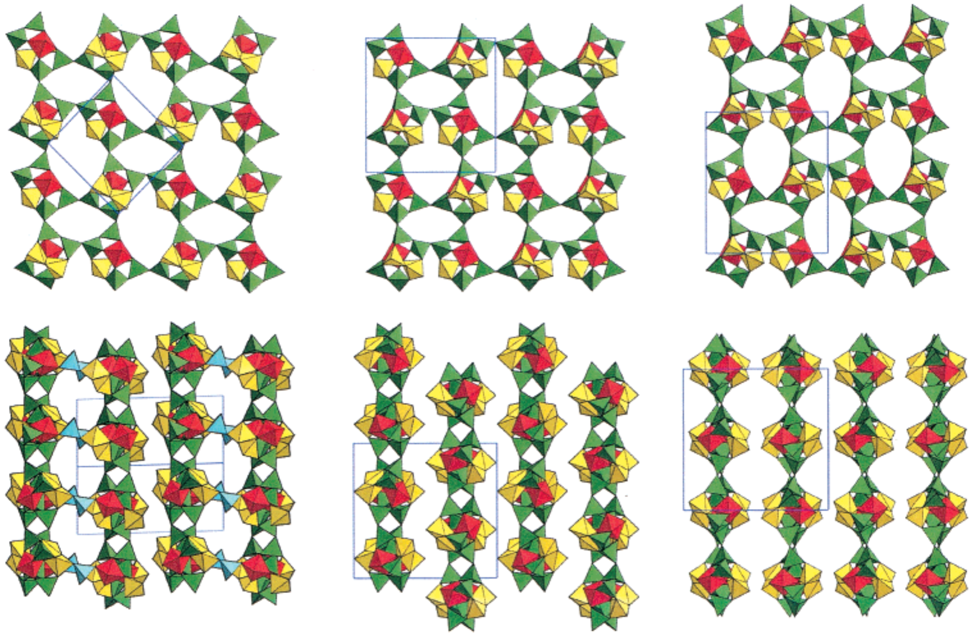
ASU-19 ASU-20-DAPe ASU-20-DACH

Figure 3. Structures of ASU-19 and ASU-20. Top: layers projected down [001]. Bottom: projected down [110] (ASU-19) and [100] (ASU-20). The Ge_7 clusters are colored as in Figure 1 and additional Ge centered tetrahedra in ASU-19 are shown in blue.

generates pores with 8- and 12-membered ring opening. The fifth bond is formed by connecting the layers pairwise through a GeO_2X_2 unit. The presence of the GeO_2X_2 spacer generates, within the double-layer of clusters, big cavities, outlined by 10- and 12-membered ring windows, with rectangular shape of dimension ca. 8 × 8 × 12 Å. The openness of the 2D slab can be better estimated using the framework density, as the non-bonded layers are closer to each other than are the bonded layers. The solid has a low framework density with 12.0 Ge atoms nm^{-3}, comparable to the framework density of ASU-12 and the less-dense zeolites. We note that linkage by GeO_2X_2 units has previously been observed in a Zn, Ge oxide structure.[12]

The structures of both ASU-20-DAPe and ASU-20-DACH consist of single layers of the same Ge_7X_{19} clusters, but now just 4-connected through tetrahedra making 8-rings. These layers (Figure 3) are similar to those combined to make the slab of ASU-19 but the orientations of the germanate clusters differ somewhat from layer to layer. The tilting in the layers is made possible by the flexibility of the inter-cluster Ge−O−Ge bond angles, the intra-cluster Ge−O−Ge angles remaining confined around an average value ca. 119°, independent of the framework topology. The Ge−O−Ge bond angle between the clusters (and the GeO_2X_2 unit) are in the range 126.5−139.5° for ASU-19 and in the range 131.9−141.8° for ASU-20-DACH. The average bond angles between germanium atoms within a cluster are $\langle Ge-O-Ge \rangle_{intra} = 119.1°$, for both ASU-19 and ASU-20-DACH with standard deviations $\sigma = 3.6°$ and $\sigma = 3.9°$, respectively. Similar values were found for ASU-12 and ASU-16. The bond distances Ge−O of the tetrahedral germanates remain within a range typical for germanium oxides. In ASU-19, d_{Ge-O} varies from 1.708 to 1.772 Å, $\langle Ge-O \rangle = 1.741$ Å, and in ASU-20-DACH, d_{Ge-O} is found between 1.725 and 1.768 Å, $\langle Ge-O \rangle = 1.746$ Å.

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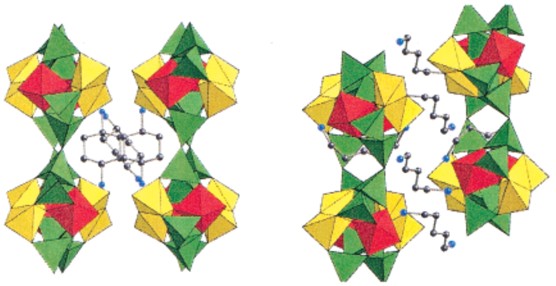
ASU-20-DACH ASU-20-DAPe

Figure 4. Position of the bases in ASU-20. Clusters illustrated as in Figures 1 and 3. Carbon, black; nitrogen, blue; hydrogen not shown.

Not only are the cluster orientations in the layers different in the two ASU-20 structures, but the layer stackings are different. In ASU-20-DAPe, the 12MR and 8MR are relatively well aligned, generating a one-dimensional system of channels along the *c* axis. On the other hand, the layers in ASU-20-DACH are staggered, an 8MR in one layer facing a 12MR in the next layer. The relative shifts of the layers along the axes *a* and *b* can be characterized by the angle β of the unit-cell and the coordinate y_{cluster} of the center of the cluster. The optimum alignment of rings along the *c* axis is obtained for $\beta = 90°$ and $y_{\mathrm{cluster}} = 0.25$. The shift of the layers is maximum along the *a* axis for β around 115°, and along the *b* axis at $y_{\mathrm{cluster}} = 0.125$; the 8MR face the 12MR at $y_{\mathrm{cluster}} = 0$. The values $\beta = 99.7°$, $y_{\mathrm{cluster}} = 0.168$, and $\beta = 109.5°$, $y_{\mathrm{cluster}} = 0.002$, are obtained for the structures of ASU-20-DAPe and ASU-20-DACH, respectively.

ASU-20 is particularly illustrative of the role played by organic bases, as the structure can be obtained using the two molecules DACH and DAPe, which differ by their size, shape, and symmetry but are found perfectly ordered within the structures (Figure 4). The envelope of DACH is more like an oblate spheroid and that of DAPe is more like that of a prolate spheroid.

Both structures contain one molecule of base in general (8-fold) position and one in special (4-fold) position, i.e., 12 per 8 Ge_7 clusters. DAPe is located within the 12MR at the site (4e) showing 2-fold symmetry. DACH, in chair configuration, is found centered on a site possessing an inversion center (4c) in the interlayer space. No DACH molecules are found within the 12MR. The linear chains DAPe, in general position, are found on top of the 8MR, on both sides of the ring, aligned along the longest diameter of the ring. Within the interlayer space, two DAPe molecules are found close together around an inversion center (4a); the shortest distance between them is ca. 3.9 Å.

A similar description holds for ASU-20-DACH. The organic base DACH is located on top of the 12MR, on both sides of the layer, aligned with the major axis of the 12MR opening. The average plane of the molecule is perpendicular to the *ab* plane. Two molecules, in the interlayer space, are found close to each other (ca. 4.1 Å for the shortest distance) and related by an inversion center (4d).

The arrangement of the layers in ASU-19 shows similarity with that of ASU-20-DAPe. Transformation of the unit-cell into the setting $C\bar{1}$ gives cell dimensions in the layer plane of $a = 16.40$ Å, $b = 16.80$ Å, and $\gamma = 86.9°$, close to the values observed for ASU-20-DAPe (Table 1). As observed in ASU-20-DAPe, one DAB molecule is located on top of the 8MR and links the two slabs together, but the 8MR faces a 12MR in ASU-19. The second DAB molecule is found within the 12MR in a general position. Both molecules are disordered, but interestingly, the disorder of the molecule within the 12MR results apparently from the presence of a pseudo inversion center.

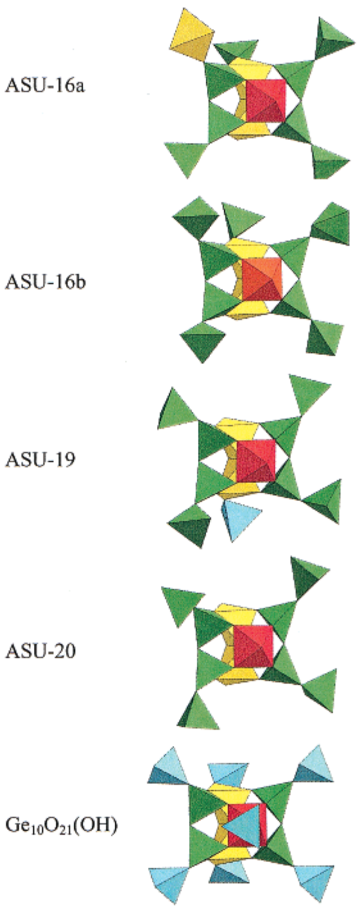

Figure 5. Mode of linking of $Ge_7(O,OH,F)_{19}$ clusters. In both ASU-12 and ASU-16 there are two distinct clusters. Tetrahedra not part of a Ge_7 cluster are shown in blue.

The two remaining DAB molecules are found ordered within the two-dimensional structure in special positions. Both molecules go through half the 10- and 12-membered rings perpendicular to the plane *ab*, with the GeO_2X_2 units pointing out into the other half.

The refinement of the structure of ASU-19 revealed that the germanium site and the two (OH, F) groups of the GeO_2X_2 unit are partially occupied with ca. 0.8 occupancy. Two OH groups or fluorine atoms attached on the clusters probably replace the GeO_2X_2 unit in its absence.

Thermogravimetry measurements revealed the departure of the organic base at a temperature ca. 250 °C, corresponding to the collapse of the structure, detected by X-ray powder diffraction at the same temperature.

The occurrence of the Ge_7X_{19} cluster and its flexibility in forming several different frameworks invites more detailed examination of its geometry. The Ge arrangement can be described as two square pyramids joined together by a triangular face, with the 13 edges symbolizing the links between the seven vertexes. The seven potentially linking Ge−O bonds of the cluster point in directions uniformly distributed in a way very similar to the optimized distribution of seven points over a sphere.[13] The center of gravity of the heptamer nearly coincides with the tri-coordinated oxygen, and all seven directions intersect at this latter point. The minimum angles between two directions of Ge−O bonds are ca. 65°. The other angles vary from 76 to 79°, quite close to the minimum angle of 78° expected in the optimized distribution. Thus, it appears that this particular combination of three different polyhedra produces a cluster, which optimizes a uniform distribution of seven Ge−O linking bonds.

The Ge_7X_{19} cluster possesses seven potentially linking Ge−O bonds and highly flexible inter-cluster Ge−O−Ge bond angles; the new materials reported here show modes of linkage different from those of the previously existing 3-D germanates.[4,5,7] Figure 5 presents a comparison of the different linkage patterns in these materials. We note that in the ASU-*n* ($n = 12$, 16, 19, and 20) materials the clusters are linked into layers with just one topological kind of cluster per layer. If we eliminate on steric grounds the possibility of nets with clusters linked into triangles, there are only four possibilities for layers with one kind of cluster, three of these, viz. 6^3 (ASU-12),[4] 4.8^2 (ASU-16),[5] and 4^4 (ASU-19, 20) have now been found, leaving just one topology, 4.6.12, yet to be achieved.

Conclusion

Three new layered compounds containing the $Ge_7(O,OH,F)_{19}$ cluster have been synthesized hydrothermally using diamines as bases. We now have six instances of extended solids containing this cluster but linked in a variety of configurations depending on the base used. It is hard to avoid the conclusion that this SBU is formed independent of the bases, whose functions are rather to direct the ternary structure (i.e., the layers and their interconnections).

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Supporting Information Available: Crystallographic data for the three phases ASU-19, DAPe-ASU-20, and DACH-ASU-20 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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