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An Open-Framework Germanate with Polycubane-Like Topology**

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The ability of germanates to form extended structures with GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra, coupled with their tendency to adopt a lower M-O-M (M = Ge) minimum angle than that of silicate-based solids, implies that a high number of possible structures with open-framework topologies can be potentially accessed.[1–3] Unexpectedly, however, only a few porous germanates have been reported thus far.[4–9] By using synthetic methods analogous to those employed for the production of zeolites and related crystalline materials,[10] we have synthesized and structurally characterized an open-framework germanate $[Ge_9O_{18}(OH)_4] \cdot 2\,H_2ppz \cdot 0.5\,H_2O$ (ASU-14, ppz = piperazine = HNC_4H_8NH), which is constructed from Ge_9 body-centered parallelepiped building blocks. These are linked together at each of their eight vertices to give the rare polycubane topology with an intersecting channel system of ten- and eight-membered rings in which the piperazinium cations and water molecules reside.

ASU-14 was prepared by heating a mixture of germanium dioxide, piperazine, water, pyridine, and HF in the molar ratio 1.0:2.4:31.0:27.7:0.80 to 165 °C for four days. A crystalline colorless solid was recovered in 76% yield (based on germanium dioxide) upon cooling this mixture. Elemental microanalysis performed on a bulk sample of this material gave the composition $[Ge_9O_{18}(OH)_4] \cdot (H_2ppz)_2(H_2O)_{0.5}$ (calcd: C 8.04, H 2.45, N 4.69, Ge 54.68, F 0.00%; found: C 7.70, H 2.47, N 4.61, Ge 53.06, F 0.19%).

An X-ray diffraction analysis of a single crystal isolated from the reaction product revealed a three-dimensional open framework constructed from the $[Ge_9O_{18}(OH)_4]$ units shown in Figure 1. A GeO_6 octahedral germanium center links two Ge_4 units that are related by an inversion center. Each of these units is constructed from a pair of GeO_4 tetrahedra and a pair of $GeO_4(OH)$ trigonal bipyramids. These are linked together through doubly bridging oxides to yield eight germanium centers that are positioned at what can be considered as the corners of a body-centered parallelepiped building block. The tetrahedral and trigonal bipyramidal Ge atoms are connected to the Ge atom at the center through doubly and triply bridging oxides, respectively. All Ge–O distances for tetrahedral germanium centers (mean: 1.734(9) Å) are similar to those reported for the quartz modification of GeO_2

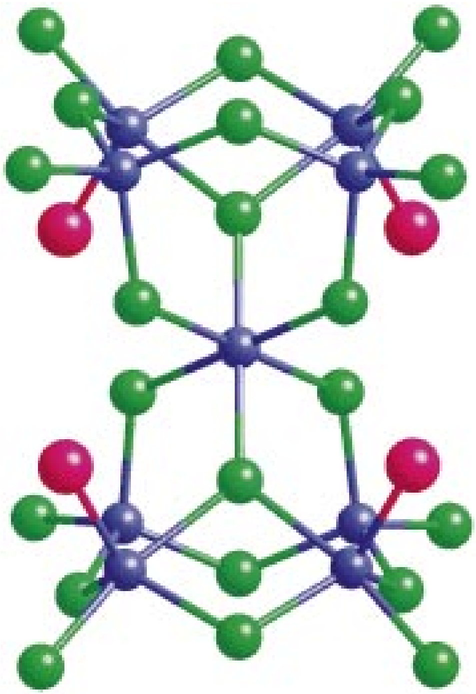

Figure 1. The building block unit present in crystalline $[Ge_9O_{18}(OH)_4] \cdot 2\,H_2ppz \cdot 0.5\,H_2O$ (ASU-14), with atoms represented by spheres: blue: Ge, green: O, pink: OH.

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(1.741(3) Å).[11] The Ge–O distances within the trigonal bipyramidal and octahedral germanium centers vary in the range 1.763(10)–2.005(9) Å, which is in general agreement with those observed in similar compounds.[4–9] However, each trigonal bipyramidal Ge atom has a terminal hydroxide ligand as evidenced by their slightly elongated Ge–OH contacts (1.779(9) and 1.763(9) Å) relative to other Ge–O(doubly bridging) distances (1.736(8) and 1.734(8) Å) in the structure, and by the presence of a sharp band at 3671 cm^{-1} in the FT-IR spectrum of this material, which is within the expected range for $\tilde{\nu}_{\text{O-H}}$ stretching frequency.[12] The remaining oxygen atoms, connected to each of the Ge atoms at the corners (one per Ge atom), serve as doubly bridging linkers to neighboring Ge_9 clusters; which thus yields an open framework with an intersecting three-dimensional channel system (Figure 2 top).

The Ge_9 units observed in ASU-14 are closely related to similar parallelepiped building blocks that can be discerned in the germanate $[Ge_{18}O_{38}(OH)_4]^{8-}$.[5] Here, instead of having four terminal hydroxide ligands linked to Ge_4 units as observed in the title compound, only two hydroxide groups act as terminal ligands while the remaining two condense to form a doubly bridging oxide that serves to link two different Ge_4 units of the same Ge_9 arrangement.

An instructive way to view the net adopted by ASU-14 involves the recognition that each of the Ge centers at the corners of the parallelepiped building blocks is in fact four coordinate, which leads to an open polycubane-like topology of the composition GeO_2 (Figure 2 bottom). This topology is a rare structural arrangement that was proposed nearly forty years ago, but only achieved recently in the porous structure of the aluminium cobalt phosphate (ACP-1) material.[13, 14] Here Co(Al)PO_4 cube units are linked at their corners into a cubic body-centered array that leads to pseudo-octagonal micropores with a diameter of 3.8 Å. Larger pores are observed in ASU-14 as a consequence of the larger size of the parallelepiped building blocks. In fact, three intersecting channels run along the crystallographic a, b, and c axes and permeate the framework with ten-, ten-, and eight-membered ring apertures with free pore diameters of nearly 5 × 6, 5 × 6, and 4 × 4 Å, respectively. The foregoing discussion of the structure requires that the framework has a charge of 4−, which is balanced by two diprotonated ppz guests that occupy the channels as confirmed by elemental microanalysis (see above). It should be noted that because of crystallographic disorder of the guests it is difficult to exclude the possibility that small amounts of solvent species such as pyridine are in the pores in addition to piperazinium cations and water. Preliminary thermal gravimetric measurements on a crystalline sample (42.37 mg) of this material showed no mass loss up to 200 °C. A gradual weight loss of 12.6 % is observed in the temperature range 200–330 °C, which is attributed to the decomposition of Hppz and liberation of water from the channels (calculated: 15.5 %). It appears that Hppz is strongly bound to the framework since a lower than expected weight loss is observed upon heating. Consequently, attempts to exchange Hppz with inorganic cations such as Na^+ and Ag^+ were not successful.

We believe that germanates offer many possibilities for the formation of cluster building blocks, which are an attractive aspect of this chemistry that is expected to yield a more extensive class of open-frameworks than that of silicate-based compounds.

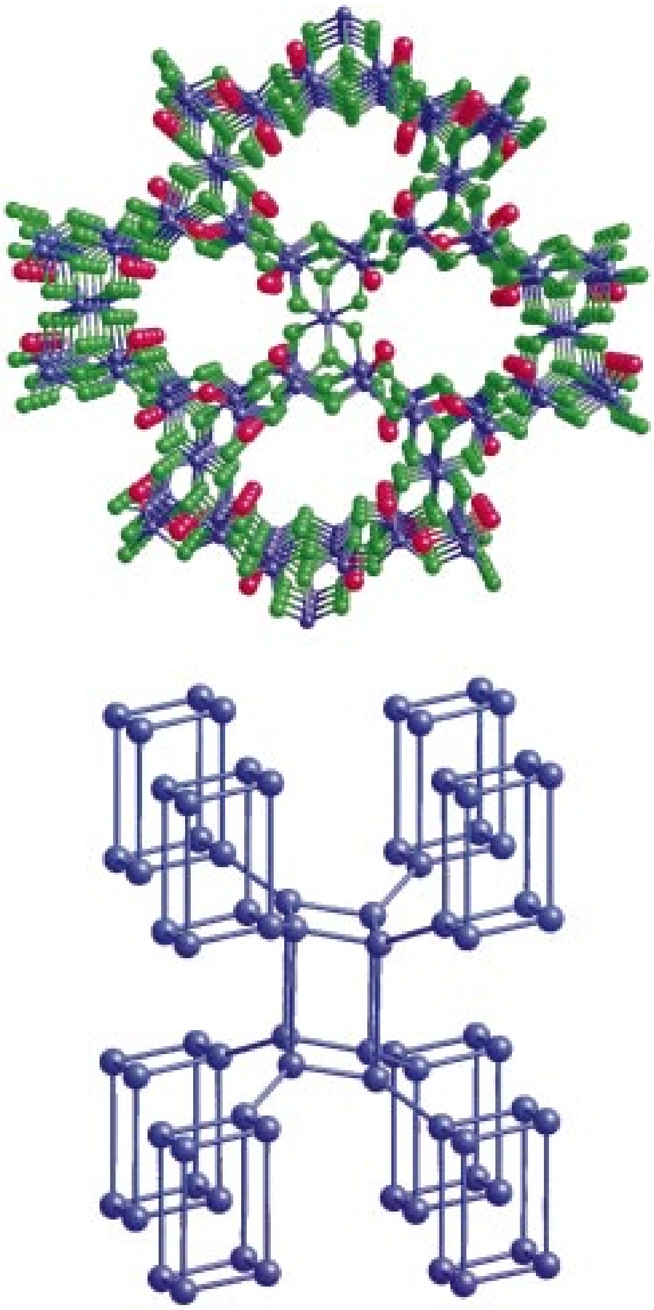

Figure 2. The crystal structure of the three-dimensional porous framework of ASU-14: top: viewed along the crystallographic b axis with all guest species omitted for clarity; bottom: a view respresenting its topology with only the four-coordinate germanium centers shown. The color code is the same as that used in Figure 1.

Experimental Section

X-ray structure analysis: Colorless columnar single crystals of $[Ge_9O_{18}(OH)_4]\cdot 2\,H_2ppz\cdot 0.5\,H_2O$ (ASU-14) were analyzed at −155 ± 1 °C, triclinic, space group $P-1$ (No. 2), $a = 10.1385(3)$, $b = 10.3465(3)$, $c = 12.8517(1)$ Å, $\alpha = 89.597(1)$, $\beta = 89.291(1)$, $\gamma = 88.923(1)°$, $V = 1347.74(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 2.870$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 99.84$ cm^{-1}. A full hemisphere of diffracted intensities ($\theta = 0.3°$ counted for a total of 10.0 s per frame) was measured with graphite-monochromated $Mo_{K\alpha}$ radiation on a Siemens/Bruker SMART CCD single crystal diffraction system. Cell constants and an orientation matrix were obtained from least-squares refinement by using the measured positions of 4386 reflections with $I > 10\sigma$ in the range $3.00 < 2\theta < 45.00°$. The Siemens/Bruker program SHELXTL-PC software package was used to solve the structure by direct methods. All stages of weighted full-matrix least-squares refinement were conducted with F_o^2 data with the SHELXTL-PC Version 5 software package and converged to give $R_1(F) = 0.062$ for 3300 independent absorption-corrected reflections with $2\Theta(Mo_{K\alpha}) < 49.5°$ and $I > 2.50\sigma(I)$ and $wR_2(F^2) = 0.069$ with a GOF = 1.70. As a consequence of the twinning found in the crystal some reflections were from the major twin only, and some were measured from both components. At the end of the refinement 87 reflections which had $Fo > Fc$ and $w\Delta F^2 > 5$ were removed from the refinement to allow all of the Ge atoms to refine anisotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114519. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Induced Color Change of Conjugated Polymeric Vesicles by Interfacial Catalysis of Phospholipase A_2**

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Conjugated polymers (CPs) such as polydiacetylene (PDA), polythiophene, and polypyrrole display a remarkable array of color transitions that arise from thermal changes (thermochromism),[1] mechanical stress (mechanochromism),[2] or ion binding (ionochromism).[1, 3] The color changes can be ascribed to a change in the effective length of conjugation of the delocalized, π-conjugated polymer backbone.[4] The application of these "smart" materials for the detection of biological targets (biochromism)[5–11] is only just beginning to be exploited.

Interfacial catalysis on biomembranes plays a key role in extra- and intracellular processes and covers a range of enzyme classes such as lipolytic enzymes, acyltransferases, protein kinases, and glycosidases. In particular, lipolytic enzymes are involved in important biochemical processes, such as fat digestion and signal transduction. Recent interest in one such enzyme, phospholipase A_2 (PLA_2),[12, 13] is motivated by its role in the release of arachidonate and lysophospholipids from membranes. These compounds are the precursors for the biosynthesis of eicosanoids (for example, prostaglandins, leukotrienes) that have been implicated in a range of inflammatory diseases such as asthma, ischaemia, and rheumatoid arthritis.[14–16] Accordingly, the identification of PLA_2 inhibitors is an active area of current research that may lead to novel therapeutics and new biochemical insights into the mechanisms of enzyme activity.[16–18]

PLA_2 catalyzes the hydrolysis of an acyl ester bond exclusively at the 2-acyl position in glycerophospholipids to

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