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The First Templated Borogermanate $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$: Linkage of Tetrahedra of Significantly Different Sizes[**]

Mike S. Dadachov,[*] Kai Sun, Tony Conradsson, and Xiaodong Zou[*]

The classes of microporous materials—tetrahedral- and mixed-framework compounds—with open structures continue to expand in terms of framework-forming elements.[1] The most accomplished and also largest classes of tetrahedral-framework compounds are aluminosilicates (Al-Si-O),[2] aluminophosphates (Al-P-O)[3] as well as their isomorphic substituted forms. Attempts to synthesize frameworks with elements other than Al, Si, and P, especially with transition metals, have resulted in many new classes, such as gallophosphates,[4] titanosilicates,[5] beryllium,[6] zinc,[7] cobalt,[8] iron,[9] vanadium,[10] nickel,[11] and molybdenum[12] phosphates. Since most transition metal atoms are too large to fit comfortably into the hole formed by a van der Waals oxygen tetrahedron, they are often coordinated by additional terminal OH and F groups, forming trigonal bipyramids, square bipyramids, or octahedra in open framework structures. As a consequence, the Me–O bonds become weaker and thus most of these compounds are thermally unstable. Besides the framework compounds containing oxygen, other compounds such as sulfides[13] and a phosphonitride[14] have been reported.

During recent years, attempts have been made to include boron atoms into the ZSM-*n* frameworks. However, very little aluminum/silicon could be replaced by boron.[15] Furthermore, a few templated metal borophosphates were reported.[16]

Open framework germanates are an interesting and expanding class of microporous materials. Germanium forms oxygen polyhedra with 4-, 5-, and 6-coordination, and germanates consisting of both purely tetrahedrally coordinated frameworks[17] and mixed polyhedral frameworks[18] have been reported.

Herein we report the synthesis and structure determination of the first templated borogermanate $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$. The hydrothermal reaction of ethylenediamine, boric acid, germanium dioxide, hydrofluoric acid, and pyridine gave transparent platelike crystals of $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ in high yield. X-ray analysis of these crystals[19] revealed a layered structure with large openings in the layers and organic templates between the layers.

There are three unique Ge and two unique B atoms in the structure, all of them tetrahedrally coordinated by oxygen atoms (Figure 1). The structure can be described as undulating borogermanate layers, each one constructed of isolated 3-rings of germanium tetrahedra, $[GeO_2]_3$, connected by pairs of boron tetrahedra, $[BO_{2.5}]_2$ (Figure 2). The borogermanate layers can also be described in terms of large 9-rings formed by alternating two-corner-linked germanium tetrahedra (six in total) and one pair of boron tetrahedra (three pairs in total) (Figure 2). The layers are connected by hydrogen bonding through the two unique charge-compensating diprotonated ethylenediamine cations. One of those cations was found to have two different conformations (Figure 1). Such behavior is not uncommon in this type of structure, since the cations reside in large cavities and possess a considerable freedom of motion.

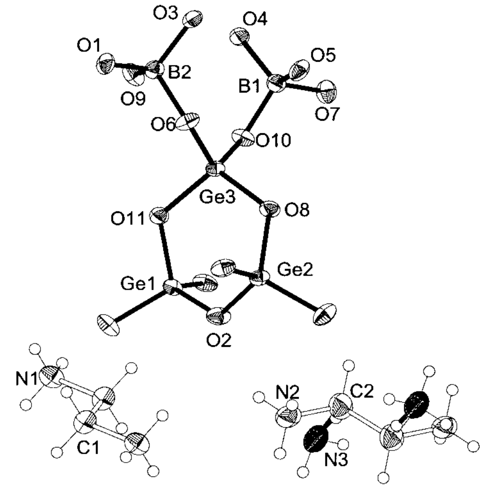

Figure 1. Atom-labeling scheme for all the non-hydrogen atoms of the asymmetric unit of $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ (ORTEP plot; 50% probability ellipsoids). The NH_3 terminal groups (N2 and N3) bonded to C2 are the two different conformations of the diprotonated ethylenediamine.

The bond lengths and angles for both the framework atoms and the guests are unexceptional. All Ge–O distances are between 1.719 and 1.768 Å and the O-Ge-O angles are between 104.27 and 115.18°. All oxygen atoms of the germanium coordination polyhedra are shared either between Ge and Ge or between Ge and B atoms. Three of the four oxygen atoms of each BO_4 tetrahedron are shared between boron and germanium, and one acts as a terminal oxygen atom pointing towards the interlayer. As a consequence, the B–O distances fall into two categories. The three bridging

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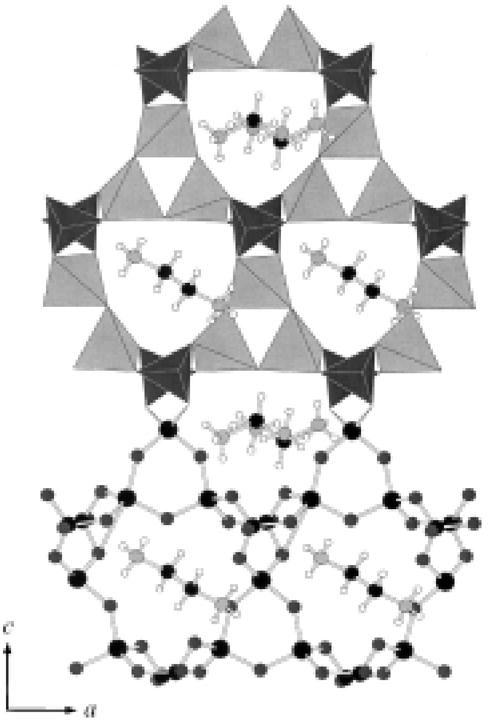

Figure 2. Polyhedral and ball-and-stick representations of the structure viewed along the *b* axis. Three GeO_4 3-rings are connected by three pairs of BO_4 tetrahedra, leading to 9-ring channels in the [010] direction. Ethylenediamine molecules are located at the center of each channel.

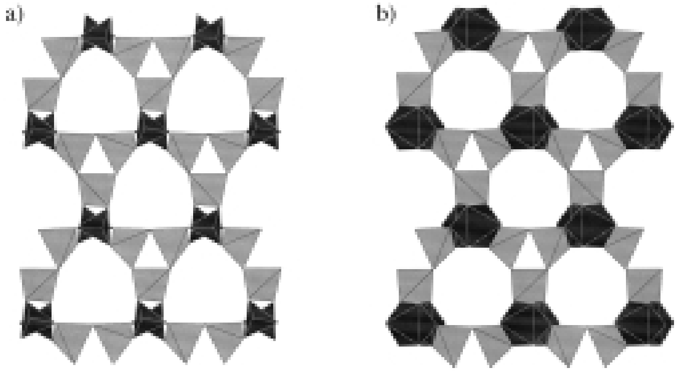

Figure 3. Comparison of the connections of the polyhedra within the layer between a) $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ and b) $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot(H_2O)_{0.67}$. GeO_4 tetrahedra are shown in light gray and BO_4 tetrahedra and GeO_6 octahedra in dark gray. The GeO_4 tetrahedra are arranged in a similar way in both structures. The only difference is that the BO_4 tetrahedral pairs in a) are replaced by GeO_6 octahedral pairs in b). Both structures contain 3- and 9-rings.

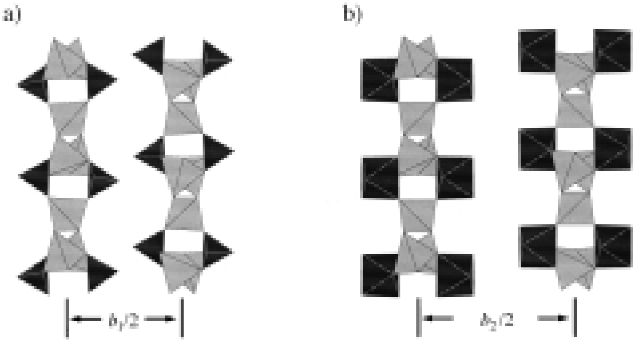

Figure 4. Comparison of the geometrical relationship between the layers. a) $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ and b) $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot(H_2O)_{0.67}$. GeO_4 tetrahedra are shown in light gray and BO_4 tetrahedra and GeO_6 octahedra in dark gray. The relative layer positions in the two structures are very similar, except that the distance between the layers in $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ $(=b_1/2)$ is shorter than in $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot(H_2O)_{0.67}$ $(=b_2/2)$. This is due to the size difference between the BO_4 tetrahedra and GeO_6 octahedra and the locations of the guest molecules in the interlayers.

B–O (–Ge) distances are practically the same (1.475(5) Å). The B–O distances to the terminal oxygen atoms are somewhat shorter (1.435(4) Å).

The radius of boron is much smaller than that of germanium. Though boron could fit into tetrahedral polyhedra, it is most commonly found to be in trigonal-planar coordination, and germanium is octahedrally coordinated by oxygen atoms. The cation-to-anion radius ratio for both B and Ge is somewhat outside the commonly observed range for tetrahedral oxygen environment. It is remarkable that they are found together in the same structure. This is probably the templated inorganic framework with the largest size difference between different tetrahedral units.

The most intriguing feature of the $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ structure is its resemblance to that of $(X)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot y\,H_2O$ ($X = NH_4$ or K, $y = 0.67-1.0$).[20–21] The structure topology within the layers is the same in both structures, except that the $[GeO_{1.5}F_3]$ octahedra are replaced by $[BO_{2.5}]$ tetrahedra (Figures 3 and 4). This replacement is nontrivial in terms of crystal chemistry, since B and Ge differ widely in valence and size. Although the $[BO_{2.5}]$ tetrahedra and the $[GeO_{1.5}F_3]$ octahedra are very different polyhedra with different sizes, they play the same structural role in the framework. The match of these very different polyhedra to the same framework can be seen by the similarity of the unit cell parameters (*a* and *c*) of these two compounds in the layer plane: $a = 7.0065$ and $c = 11.7976$ Å for $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot(H_2O)_{0.67}$ and $a = 6.9765$ and $c = 11.6943$ Å for $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$. The relative position of the two adjacent layers is very similar in both structures (Figure 4), even though different molecular and ionic species are present in the interlayers. The interlayer distances are different in the two structures, however, due to the size differences of the $[BO_{2.5}]$ tetrahedra and $[GeO_{1.5}F_3]$ octahedra, and the different locations of the intercalated species of ethylenediamine and ammonium cations and water. The $[BO_{2.5}]^{2-}$ and $[GeO_{1.5}F_3]^{2-}$ units, which are the only negatively charged parts of the framework layers, are compensated by the diprotonated ethylenediamines and ammonium cations in $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ and $(NH_4)_4[(GeO_2)_3(GeO_{1.5}F_3)_2]\cdot(H_2O)_{0.67}$, respectively.

We have shown for the first time that boron can be incorporated into templated germanate frameworks. This opens possibilities for synthesizing other templated borogermanates with novel structure topologies.

Experimental Section

Crystals of $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$ were synthesized from an organic-rich solution consisting of ethylenediamine, H_3BO_3, GeO_2, HF, pyridine, and H_2O in a molar ratio of 12:2:1:2:40:5. GeO_2 (0.15 mg) was added to a mixture of pyridine (4.55 g) and water (0.147 g). Then ethylenediamine (1.038 g) was added and stirred until the mixture became a clear solution. Finally boric acid (0.18 g) and 40% HF (0.062 g) were added to the obtained solution (pH 11.12), which was then heated at 170°C for 10 days in a 23 mL Teflon-lined Parr autoclave. The product (yield 0.206 g), consisting of a white powder and thin platelike single crystals, was collected, washed with deionized water and ethanol, and dried at room temperature. The Ge content was confirmed by energy-dispersive spectroscopy (EDS).

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[19] X-ray structure analysis: STOE IPDS system with image plate; graphite monochromator; $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å; $T = 293$ K; the structure was solved by using the direct-method routine of SIR-97[22] and refined by full-matrix least-squares methods using SHELXL-97;[23] numerical absorption correction by X-RED[24], $T_{\min} = 0.4281$, $T_{\max} = 0.8850$. Crystal data for $(C_2N_2H_{10})_2[(BO_{2.5})_2(GeO_2)_3]$: crystal dimensions $0.10 \times 0.10 \times 0.02$ mm, monoclinic, space group $P2_1/n$, $a = 6.9765(9)$, $b = 14.4103(12)$, $c = 11.6943(14)$ Å, $\beta = 91.093(15)°$, $V = 1175.46(23)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.69\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 76.833\ \mathrm{cm^{-1}}$, $2\theta_{\min} = 6.4°$, $2\theta_{\max} = 47°$, $R_1 = 0.034$ for 1525 reflections with $F_o > 4\sigma(F_o)$ and 0.039 for all 1729 reflections, $wR_2(F^2) = 0.095$, GOF = 1.136, 194 parameters were refined, max./min. residual electron density $-0.79/0.86$ e Å^{-3}. One of the $(H_3NCH_2CH_2NH_3)^{2+}$ ions was found to have two different conformations (Figure 1). This was refined as the N-population parameters of the N2 atom at two sites as 0.73 and 0.27. All other parameters are unexceptional. Most of the hydrogen atom positions could be located on the final difference Fourier maps, and they were introduced by the rigid-group riding mode, allowing refinement of their isotropic thermal parameters. 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-143794. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Dodecacarbonyltetracobalt Catalysis in the Thermal Pauson – Khand Reaction**

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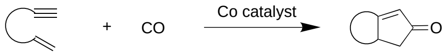
Dicobaltoctacarbonyl, $[Co_2(CO)_8]$, has always been the metal complex of choice in the widely used Pauson – Khand reaction for the formation of bicyclo[3.3.0]octenones by the cyclocarbonylation of an alkene and an alkyne (Scheme 1).[1] Alternative sources of zero valent cobalt, namely [(indenyl)Co(cod)] and $[Co(acac)_2]/NaBH_4$, and cobalt carbonyl clusters, such as $[Co_4(CO)_{12}]$, $[Co_3(CO)_9(\mu_3\text{-}CH)]$, and $[Co_4(CO)_{11}P(OPh)_3]$, have also been developed but are less



Scheme 1. Cobalt catalysis in the Pauson – Khand reaction. Co catalyst: $[Co_2(CO)_8]$ with or without additive (phosphite, phosphane, cyclohexylamine ($CyNH_2$), phosphane sulfide, 1,2-dimethoxyethane (DME), water), $[Co_4(CO)_{12}]$, $[Co_4(CO)_{11}P(OPh)_3]$, $[Co_3(CO)_9(\mu_3\text{-}CH)]$, [(indenyl)Co(cod)], $[Co(acac)_2]/NaBH_4$. cod = cycloocta-1,4-diene; acac = acetylacetonate.

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