atoms were included in the ideal positions with fixed isotropic values. Calculations were performed using the programs TEXSAN (data reduction) and SHELX-97 (refinement).

[33] ^{1}H NMR spectroscopic analysis of **2** in chloroform solution at a 17-mM concentration indicated that **2** assembles to form the two expected dimeric assemblies as evidenced by two sets of hydrogen-bonded NH resonances, corresponding to two distinct sets of homophenylalanine and phenylalanine residues. Upon examination at low temperature, an additional set of hydrogen-bonded NH protons appeared possibly arising from a dimer desymmetrized by cross-strand aryl–aryl interaction, though subsequent two-dimensional ^{1}H NMR spectroscopic investigation was inconclusive (see Supplementary Information).T. D. Clark, J. M. Buriak, K. Kobayashi, M. P. Isler, D. E. McRee, M. R. Ghadiri, *J. Am. Chem. Soc.* **1998**, *120*, 8949–8962.

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A Large 24-Membered-Ring Germanate Zeolite-Type Open-Framework Structure with Three-Dimensional Intersecting Channels[**]

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The search for new topological microporous structures of extra-large-pore open frameworks with more than 12 tetrahedral atoms has been extremely intensive because of the widespread applications of these materials in catalysis and the separation of large molecules such as heavy oils or pharmaceuticals. Since the first molecular sieve containing 18-membered rings (18MR), aluminophosphate VPI-5, was discovered in 1988,[1] many metal phosphates and aluminosilicates with extra-large-pore open frameworks such as $AlPO_4$-8 (14MR),[2] Cloverite (20MR),[3] JDF-20 (20MR),[4] UTD-1 (14MR),[5] CIT-5 (14MR),[6] ND-1 (24MR)[7] have been synthesized. Several useful synthetic approaches have been studied to prepare such large-pore materials.[8] Among these are, for example, the use of large templates, the selection of framework elements that can form three-membered rings, such as the zincosilicates and zincophosphates,[9] or the use of tailored secondary building units (SBUs), for example, in the preparation of large-pore indium sulfide.[10] However, most of the materials with extra-large-pore frameworks have only one-dimensional (1D) channels. Germanates are of particular interest because they can form extended structures with GeO_5 trigonal bipyramids or GeO_6 octahedra, as well as GeO_4 tetrahedra.[11, 12] The high coordination numbers offer the possibility of synthesizing germanate frameworks with high charge densities, which may result in multidimensional channel systems and novel structures with large pores.[13] Unfortunately, to date extra-large-pore germanate zeolite-type structures have not been successfully prepared. According to the host–guest charge-matching concept,[14, 15] a highly charged inorganic framework should be templated by highly charged organic amines such as multiamines. Herein we report the synthesis and structure of the unique germanate zeolite analogue **1** (known as FDU-4) with a large 24-membered ring. Compound **1** was prepared by using an organic multiamine, tris-(2-aminoethyl)-amine (TREN) as a structure-directing agent in a *N*,*N*-dimethylformamide (DMF)/water mixture. Interestingly, the novel germanate open-framework structure has a three-dimensional (3D) intersecting channel system, in which each 24MR channel is surrounded by six 12MR channels, and the 12MR and 24MR channels are connected by the alternating 8MR pore windows.

$$[Ge_9O_{17}(OH)_4][N(CH_2CH_2NH_3)_3]_{2/3}\,[HCON(CH_3)_2]_{1/6}\,(H_2O)_{11/3} \qquad \textbf{1}\ \text{(FDU-4)}$$

FDU-4 is the first germanate zeolite-type structure with the 24-member ring channels and it has a previously unknown framework topology with the space group $P6_3cm$ (No. 185, standard setting). A single-crystal X-ray diffraction analysis reveals the 3D open framework constructed from the SBU shown in Figure 1. The core of the SBU has C_{2v} symmetry and is composed of nine germanium centers, seventeen oxygen

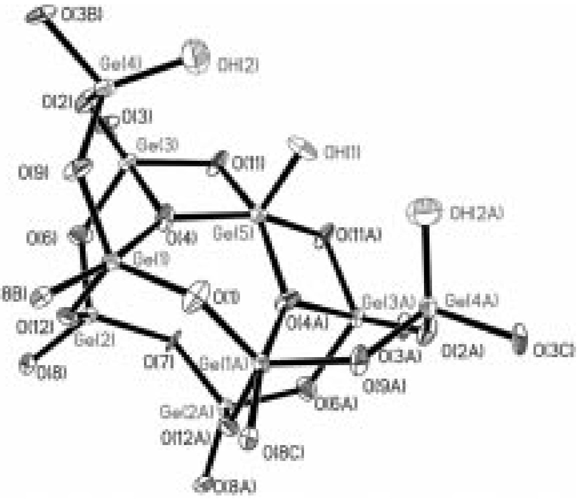

Figure 1. ORTEP view of the building block unit in crystalline FDU-4. Atoms labeled A, B, or C are symmetry generated.

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centers, and four OH units. A germanium center (Ge(5)) lies on the mirror plane, and is bound to five oxygen centers to yield a distorted square pyramid coordination geometry. Four germanium atoms (Ge(1), Ge(1A), Ge(3) and Ge(3A)) are each bonded to five oxygen atoms to give trigonal bipyramidal coordination, the remained four germanium atoms (Ge(2), Ge(2A), Ge(4), and Ge(4A)) have distorted tetrahedral coordination geometries. However, Ge(4), Ge(4A), and Ge(5) connect three terminal oxygen atoms belonging to hydroxide ligands, the presence of which is confirmed by the presence of a sharp FT-infrared (IR) band at 3730 cm^{-1} in the expected range for ν_{O-H} stretching frequencies. An intriguing feature of the FDU-4 structure is its relation to that of some previous germanates, such as ASU-12 and ASU-14[12]. They all contain tricoordinate oxygen centers connected to three different five- or six- coordinate Ge centers. Three-coordinate oxygen centers favor not only trigonal bipyramidal or octahedral geometry but also three-membered rings,[15] and such a structural feature is believed to be the key to frameworks with the lowest possible framework density.[16] The framework density of FDU-4 measured by the number of polyhedra per 1000 $Å^3$ is 11.1, which is one of the lowest framework densities known.

All the Ge–O bonds for the tetrahedral Ge centers (mean 1.738(6) Å) are very similar to those reported for the quartz modification of GeO_2 (1.741(3) Å).[17] The Ge–O bonds of the five-coordinate Ge centers are in the range 1.753(5)–2.163(5) Å, in agreement with those observed for other germanates.[11, 12, 18]

Neighboring SBUs are linked by bridging oxygen atoms to yield an open framework with an intersecting 3D channel system. There are two kinds of channels with 12 and 24 members, extending along the crystallographic *c* axis (Figure 2). Although the two kinds of channels have different sizes, they can be arranged in close-packed hexagonal, honeycomb arrays, just as in the mesoporous materials MCM-41 or SBA-15.[19] Each 24MR channel is surrounded by six 12MR channels and these are alternately surrounded by three 12MR channels and three 24MR channels. The approximate diameters of the narrowest cross section of the 24MR and 12MR channels are 12.65 Å and 9.52 Å, respectively. The results imply that the formation of mesoporous materials with two uniform, ordered, pore channels or/and microporous crystalline walls similar to the structure of FDU-4 is possible. The wall of the 12MR channels of FDU-4 is composed of a 4,8,8 net with alternating 4MR and 8MR (Figure 3a). The 8MR channels run in three directions perpendicular to the *c* axis, and cross at an angle of 120°. The wall of the 24MR channels includes 12MR windows (Figure 3b) resulting in an unprecedented 3D intersecting-channel germanate framework.

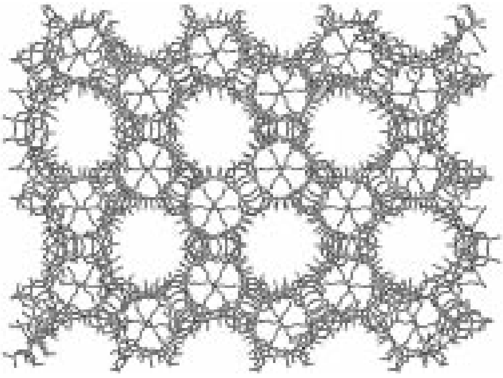

Figure 2. Projection of the 3D framework down the *c* axis in FDU-4. The DMF and water guests are omitted for clarity.

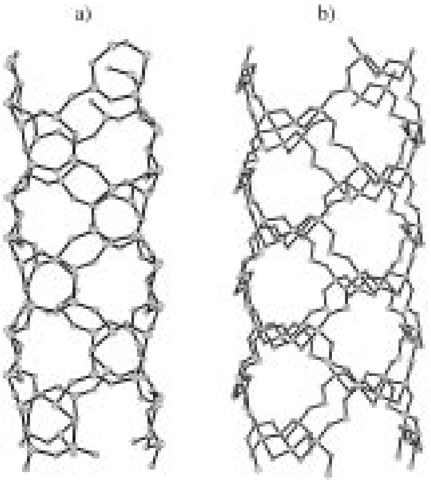

Figure 3. a) 12MR channel view normal to the [001] direction; b) 24MR channel view normal to the [001] direction.

The organic amine molecules in FDU-4 are located within the 12MR channels (Figure 2) and form hydrogen bonds with the framework oxygens. Some solvent species such as DMF (1/6 molecule per SBU) and water molecules (11/3 H_2O per SBU) are disordered and located in the 24MR channels. The presence of DMF is also confirmed by the sharp FT-IR band at 1601 cm^{-1} correspond to $\tilde{\nu}_{C=O}$ stretching frequency. These results suggest that the large-pore channels do not need to be templated by large molecules, which is similar to the case in VPI-5.[1] The structure requires that the framework has a 2– charge per SBU, which should be balanced by 2/3 triprotonated TREN. This implies that there is one bridging hydroxide [Ge-O(H)-Ge] per SBU in the framework. We believe that O(8) and O(8A) could be protonated with an occupancy of 0.5 because of their elongated Ge–O bonds (av 1.797 Å) and their low thermal parameter (0.016).

Preliminary thermogravimertric and differential thermal analyses for a crystalline sample of this material show three weight-loss steps accompanied by three endothermic peaks. One weight loss (7.5%) between 100°C and 240°C corresponds to the loss of H_2O and DMF (calculated 6.7%). Another weight loss of 8.2% between 280°C and 380°C is attributed to decomposition of H_3TREN (calculated 8.5%). After 380°C, a gradual weight loss of 4.5% until 700°C is observed and assigned to the loss of terminal OH groups from the framework (calculated 4.3%). Powder X-ray diffraction measurements show that the structure of FDU-4 collapses after heating at 400°C for 3 h, suggesting that the large-pore structure is unstable.

Experimental Section

Compound **1** was synthesized by using mixture of DMF and water as the solvent, and TREN as a structure-directing agent. A reaction mixture containing GeO_2 (0.413 g, 3.95 mmol), TREN (2.35 g, 16.1 mmol), water (5.01 g, 278 mmol), DMF (8.01 g, 110 mmol) was stirred at room temperature over night. The mixture was heated at 180 °C in a Teflon-lined steel autoclave for seven days. Colorless needlelike crystals were obtained in approximately 70 % yield (based on GeO_2).

X-ray structure analysis: Needlelike single crystals of FDU-4 ($0.20 \times 0.03 \times 0.04$ mm) were analyzed at room temperature. Crystallographic data for FDU-4: hexagonal, space group $P6_3cm$ (No. 185), $a = 23.941(3)$, $b = 23.941(3)$, $c = 9.798(2)$ Å, $V = 4863.2(14)$ Å^3; $Z = 6$; $\rho_{calcd} = 2.399$ g cm^{-3}, $F(000) = 3360$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å. A full hemisphere of diffracted intensities was measured with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation on a Bruker/Siemens Smart1000-CCD. Of 22955 reflections collected, 4681 were independent ($R_{int} = 0.1347$). Cell constants were obtained from least-squares refinement in the range $0.98 < \theta < 23.34°$. The Siemens/Bruker program SHELXTL-PC software package was used to solve the structure by direct methods. Refinement was by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. The final residuals were $R_1(F) = 0.0606$ with $I > 2\sigma$ and $wR_2(F^2) = 0.1551$ with GOF$(F) = 1.050$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151489. 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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Formation of Aryl- and Benzylboronate Esters by Rhodium-Catalyzed C–H Bond Functionalization with Pinacolborane**

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The catalytic functionalization of unreactive C–H bonds remains one of the major challenges in chemistry.[1] Metal–boryl systems have been shown to promote stoichiometric[2] and photocatalytic[3] conversion of alkane and arene C–H bonds into C–B(OR)$_2$ groups by using B_2pin_2 (pin = OCMe$_2$CMe$_2$O). A [Cp*Ir] complex catalyzes[4] the borylation of benzene with pinacolborane (HBpin), with about three turnovers obtained at 150 °C, and a related complex [Cp*Rh(η^6-C_6Me_6)] is an excellent catalyst[5] for aliphatic and aromatic C–H bond borylation at 150 °C, with B_2pin_2 being more effective than HBpin. As part of our studies of the reactivity of B–H bonds with Rh and Ir complexes,[6] we report herein that [RhCl(P*i*Pr$_3$)$_2$(N$_2$)] (**1**)[7] is an efficient catalyst precursor for the borylation of aromatic and benzylic C–H bonds with HBpin, and that high selectivity for benzylic C–H functionalization was observed for the first time with toluene, *p*-xylene, and mesitylene. The boronate ester products represent an important class of synthetic intermediates.[8]

The reaction of 0.2 M HBpin[9] with benzene in the presence of 1.0 mol% of **1** at 140 °C gave PhBpin in 62 % yield (62 turnovers) after 14 h and in 86 % yield after 58 h (Scheme 1). When 0.3 mol% of **1** was used, 67 % (222 turnovers) of PhBpin was obtained after 104 h. The yield improved at lower HBpin concentrations. Thus, with 1.0 M HBpin in benzene, PhBpin was obtained in 20 % yield after 58 h, whereas dilution with hexane (fourfold) improved the yield to 35 % in the same time. This effect can be attributed to degradation of HBpin, which is strongly concentration dependent.[10] In addition to PhBpin, the dehydrodimerization product B_2pin_2 was formed, especially with higher concentrations of HBpin (ca. 7 % for 1.0 M HBpin in benzene).

Toluene was less active than benzene, indicating that the methyl group deactivates the arene C–H bonds (Table 1, entry 1). Interestingly, the main product, PhCH$_2$Bpin, was not

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.