$(NH_4)_2Ge_7O_{15}$: A Microporous Material Containing GeO_4 and GeO_6 Polyhedra in Nine-Rings**

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Crystalline microporous materials are widely used in the fields of catalysis, ion exchange, and adsorption. Since the first discovery of zeolites, many natural and synthetic zeolites,[1–7] silica polymorphs, aluminophosphate-based molecular sieves,[8–11] and microporous compounds built from MO_4 tetrahedra where the M centers are atoms other than aluminum or silicon[12] have been synthesized.

Like silicon, germanium atoms tend to be surrounded by a tetrahedron of oxygen atoms, which may join through shared corners to form larger units; in fact, some compounds of the two elements are isomorphous. However, in Ge zeotypes the structure of the framework can be formed by GeO_4 tetrahedra, GeO_6 octahedra, and sometimes even GeO_5 trigonal bipyramids.[13] For this reason it is surprising that few reports of microporous germanates exist in the literature. To our knowledge, the only fully characterized compounds are of the type $M_{3+x}H_{1-x}Ge_7O_{16}\cdot nH_2O$ (M = monovalent cation) with pharmacosiderite-type structure, obtained by ion exchange from the compounds $(NH_4)_3HGe_7O_{16}\cdot nH_2O$,[13–20] $[Ge_6O_{12}(OH)]^-[N(CH_3)_4]^+$[21] and $[Ge_{18}O_{38}(OH_4)]^{8-}[(C_2N_2H_{10})^{2+}]_4$.[22] All of them have the framework structure of zeolites and show many of their properties.

An extremely interesting question is whether different germanium dioxide frameworks can be obtained by changing the ratio of GeO_6 octahedra to GeO_4 tetrahedra while using the same template. In other words, can different phases be obtained inside the GeO_2/NH_4^+ system? In this paper we report the first results of our effort: the novel zeolite-like germanate, $(NH_4)_2Ge_7O_{15}$, containing octahedra and tetrahedra forming nine-rings, an arrangement that has never been observed before in microporous solids. Thus, this material could display new effects of shape selectivity in catalytic processes and offer unique properties as molecular sieves.

The title compound was synthesized hydrothermally from a reaction mixture containing GeO_2, $NH_4(OH)$, H_2O, and ethylene glycol in the molar ratio 1:0.6:30:12 on heating at 180°C for 14 days. The cubic and prismatic crystals observed in the resulting solid product were identified as $(NH_4)_3HGe_7O_{16}\cdot nH_2O$ and a new unknown phase, respectively. Figure 1 shows the X-ray diffraction patterns for both the cubic and the new microporous germanates.

A suitable single crystal of prismatic shape was selected and mounted in a diffractometer equipped with a CCD detector. The crystal structure (see Experimental Section) indicated that the composition is $(NH_4)_2Ge_7O_{15}$, in which six Ge atoms are tetrahedrally coordinated [range of Ge–O bond lengths 1.715(4)–1.782(4) Å; O-Ge-O bond angles 106.7(2)–116.1(2)°], and the remaining one is octahedrally coordinated to oxygen atoms [range Ge(4)–O bond lengths 1.863(4)–1.923(3) Å; bond angles between 86.2(2) and 93.8(2)°]. Therefore, in the unit cell there are 28 Ge atoms, 60 oxygen atoms, and 8 NH_4^+ ions.

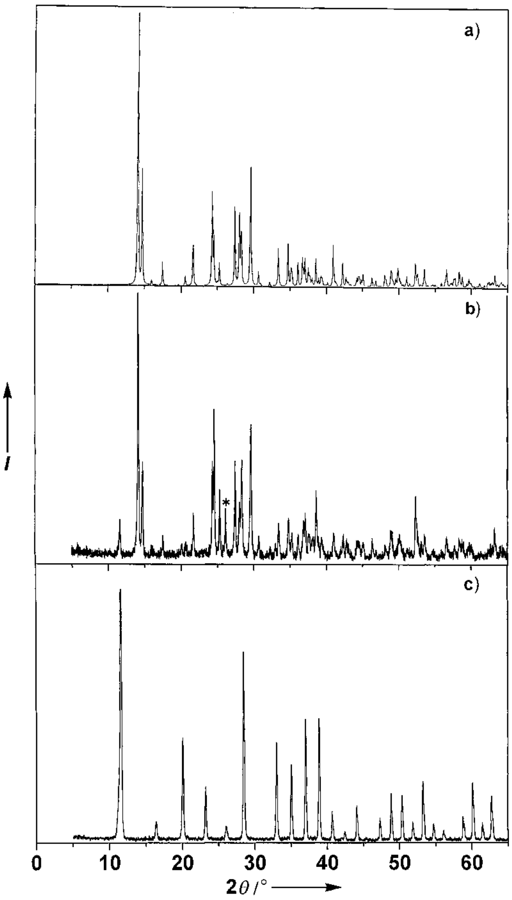

Figure 1. X-ray powder diagrams (XPD) a) calculated for $(NH_4)_2Ge_7O_{15}$ XPD from single-crystal structure data, b) recorded for the obtained material (* corresponds to the higher GeO_2 peak), and c) recorded for $(NH_4)_3HGe_7O_{16}\cdot 4H_2O$. I = intensity (arbitary units)

Tetrahedra and octahedra are linked by sharing corners in such a way that each tetrahedron is surrounded by one octahedron and three tetrahedra, and each octahedron is surrounded by six tetrahedra. The structure can be envisaged in terms of a two-dimensional sheet that is repeated to generate the full three-dimensional structure. This sheet is perpendicular to the *c* axes and is formed by nine-polyhedra rings (seven are tetrahedra and two are octahedra) in a 4Td-Oh-3Td-Oh sequence (Figure 2). This arrangement forces the formation of parallel double rings, which are held together through the octahedra and create some thickness to the layer. The shape of the ring is nearly a regular triangle.

This sheet, which is repeated by vertical translation along the stacking *c* direction, is bonded to the neighboring sheets located directly above and below through the only vertex of the tetrahedra not involved in connectivity inside the layer. As explained before, the octahedra are inside the sheet forming the double rings. This sort of packing gives rise to three types of channels, in all of which GeO_6 octahedra are

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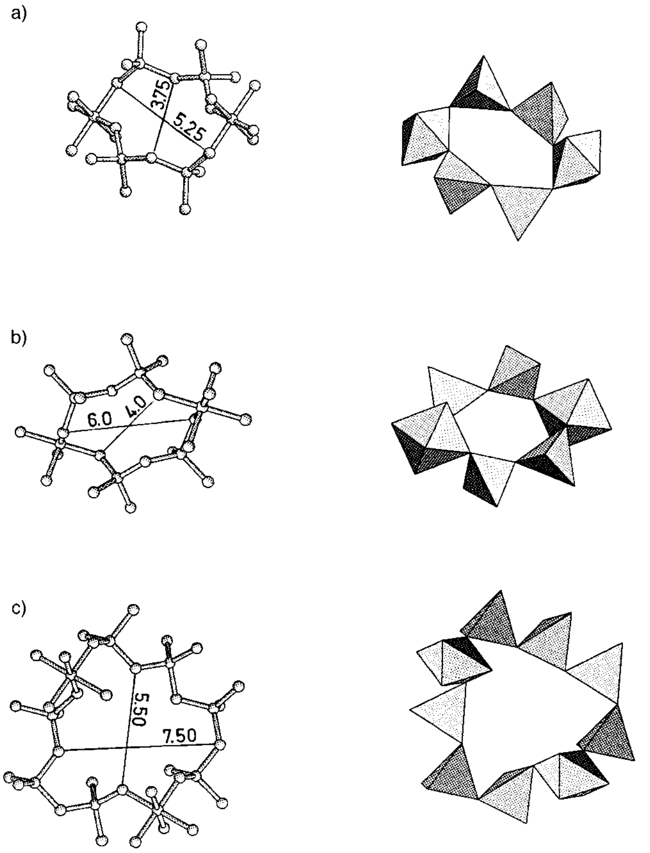

Figure 2. Ball-and-stick and polyhedral representations of the windows corresponding to the three different kinds of channels present in the structure of $(NH_4)_2Ge_7O_{15}$ along [110] (a), [010] (b), and [001] (c). Distances to the centers of atoms are given.

involved. The main channels are those that run in the *c* direction as a consequence of the stacking of the nine-rings. There are smaller hexagonal channels along [010] and [110] with a $2(GeO_4)$-(GeO_6)-$2(GeO_4)$-(GeO_6) sequence. Pore apertures and sizes are also shown in Figure 2.

Two NH_4^+ cations, whose positions are related by a inversion center, are guests in each cage along the main channels (Figure 3). Since every H atom was located in a difference synthesis and their coordinates refined with isotropic thermal parameters, the whole geometry around H bonds could be determined. The NH_4^+ cation is bonded to different oxygen atoms of the framework through the four hydrogen atoms; three of these atoms form bifurcated hydrogen bonds. The ranges of the N–H, N–O, and O–H bond lengths are 0.78(2)–1.05(1) Å, 2.631(5)–3.106(6) Å, and 1.82(1)–2.51(1) Å, respectively.

A comparison of the coordination polyhedra and their connectivities present in the cubic $(NH_4)_3HGe_7O_{16} \cdot n\,H_2O$ (structural type I), the $Ge_9O_{20}Na$ structure (structural type II),[23] and the new monoclinic $(NH_4)_2Ge_7O_{15}$ (structural type III) reveals a number of interesting features. Although the frameworks are always formed by GeO_4 tetrahedra and GeO_6 octahedra, the ratio GeO_4/GeO_6, which is 3/4 for I and 5/4 for II, is 6/1 in III. This composition avoids the formation of the Ge_4O_{16} cluster, which is present in I and II, and brings about the formation of tunnels of different sizes, creating a main channel and thus a preferential direction for ionic conductivity. In other tunnel-containing materials that are good ionic conductors[24] the amplitude of thermal vibration of the ions in the direction of the tunnels is associated with an unhindered motion of those cations and with high ionic conductivity. In this new germanate, although the NH_4^+ cations are involved in hydrogen bonds, the anisotropic thermal parameters of the N atom is especially large in the *c* direction (about twice as large: $U_{11} = 20(4) \times 10^{-3}$, $U_{22} = 20(3) \times 10^{-3}$, and $U_{33} = 44(4) \times 10^{-3}$). Moreover, in the title compound the formal charge of the framework is compensated by two NH_4^+ cations per seven Ge atoms, which decreases the electrostatic interaction between the anion framework structure and the cations. In contrast, for the same number of Ge atoms in I, four cations are needed.

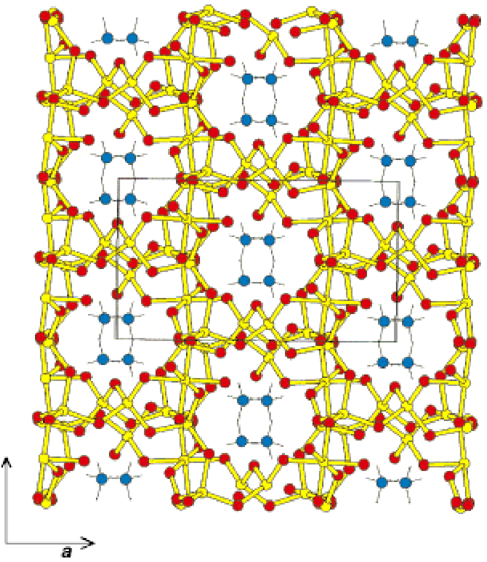

Figure 3. View along [001] of the structure of $(NH_4)_2Ge_7O_{15}$. The NH_4^+ ions are in blue.

TGA-DTA (TGA = thermogravimetric analysis, DTA = differential thermal analysis) shows a 4% weight loss between 320 and 450°C, which is endothermic. This corresponds to the total decomposition of the $(NH_4)_2Ge_7O_{15}$ present in the sample (70% $(NH_4)_2Ge_7O_{15}$ and 30% GeO_2) by loss of one H_2O and two NH_3 molecules. Powder X-ray diffraction measurements show that the structure is maintained after heating to 312°C and collapses at 450°C to crystalline GeO_2.

As $(NH_4)_2Ge_7O_{15}$ is stable 100°C above the temperature limit for $(NH_4)_3HGe_7O_{16} \cdot n\,H_2O$,[16] we can obtain the monoclinic phase free of the cubic one by heating at 250°C for two hours. This material thus has an advantage for potential applications.

The charged framework of this material contains no Ge–OH group, which is present in analogous materials,[21–22] and therefore, besides potential use as a solid electrolyte, it might be possible to make this material acidic and thus catalytically active. Relative to silica molecular sieves and clathrates, this novel compound seems to have a unique structure: the interaction between GeO_4 and GeO_6 anion framework structure and the cations in the channels is weaker than the one between the tetrahedral anionic network of zeolites and their cations.

Experimental Section

X-ray structure analysis: Crystal dimensions 0.020 × 0.015 × 0.015 mm. Monoclinic, space group $C2/c$, $a = 13.056(2)$, $b = 7.2941(9)$, $c = 15.162(2)$ Å, $\beta = 103.575(2)^\circ$, $V = 1403.6(3)$ Å^3, $Z = 4$, $M_w = 784.2\ \text{g mol}^{-1}$, $\rho_{calcd} = 3.711\ \text{g cm}^{-3}$, $F(000) = 1{,}464$. CCD Siemens diffractometer (sealed tube, 2.4 kW), $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $\mu_{K\alpha} = 14.87\ \text{mm}^{-1}$; of 2611 reflections measured, 1002 were independent ($R_{int} = 0.0547$), $2 < \theta < 23.5^\circ$. Structure determination and refinement software SHELXTL.[25] All the hydrogen atoms were located in the difference Fourier maps. The 114 variables were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms and isotropic for hydrogen atoms. The final residuals were $R_F = 0.024$ for $F > 4\sigma(F)$ and 0.027 for all data, GOF$(F) = 1.167$. Further details of crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344, Eggenstein-Leopoldshargen (Germany), on quoting the depository number CSD-407222. Patent Registry No. $(NH_4)_2Ge_7O_{15}$ 9700705.

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Double-Helical Oligo Esters: Chiral Twist of Two Aromatic Ester Chains

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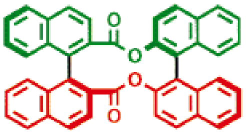
The double-helical structure is often found in nature, and artificial double-helical molecules are also of interest; for instance, in 1991 Lehn and co-workers prepared a double-helical structure by utilizing the coordination of nitrogen atoms of two chains to copper ions.[1] In another example, two chains are bound by hydrogen bonds of an oligopeptide.[2] However, in contrast to these approaches based on self-assembly, covalent bonds have been used less frequently in the synthesis of such molecules. Here we report the preparation of oligo esters **2** and **3**. In these molecules, biphenyl groups are sandwiched between two chiral binaphthyl groups. Through this "chiral twist", the originally achiral biphenyl groups are fixed in the same absolute configuration as the two binaphthyl groups on both ends. As a result, the two oligo ester chains in one molecule (green and red in **1**–**3**) are twisted to form a double-helical structure.[3]



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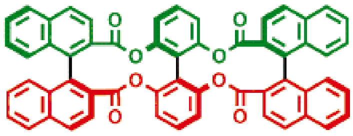

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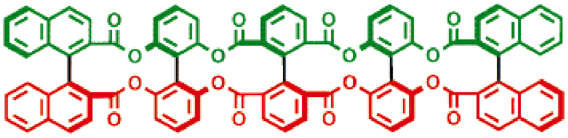

3

For the synthesis of these compounds (*S*)-1,1′-binaphthyl-2,2′-dicarbonyl dichloride was initially treated with biphenyl-2,2′,6,6′-tetrol (Scheme 1), which gave the 1:1 coupling product **4a** and the 2:1 product **2** in 41 % and 54 % yield, respectively. It is noteworthy that **4a** was obtained as a single diastereomer although two diastereomers **4a** and **4b** could have formed. Biphenyl-2,2′,6,6′-tetrol itself is an achiral molecule. After the first esterification of the 2-hydroxy group, the two hydroxy groups at the 2′- and 6′-positions are diastereotopic. Thus the second esterification step proceeds exclusively at one of these two hydroxy groups.

The absolute configuration of the biphenyl group was determined by the following method: The two hydroxy groups of **4a** were protected as methyl ethers, and then the compound was hydrolyzed to give the 2,2′-dimethoxybiphenyl-6,6′-diol (**5**) and 1,1′-binaphthyl-2,2′-dicarboxylic acid (Scheme 2). The

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