

(1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2 H₂O: A New Microporous Germanate Based on the Interconnection of Ge₃O₁₈ Clusters Showing Reversible Water Emission and Uptake

Dragan Pitzschke, Christian Näther, and Wolfgang Bensch

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel,
Olshausenstraße 40, D-24098 Kiel, Germany

Reprint requests to Prof. Dr. Wolfgang Bensch. Fax: +49-(0)431-880-1520.
E-mail: wbensch@ac.uni-kiel.de

Z. Naturforsch. **58b**, 205 – 210 (2003); received October 17, 2002

Treatment of germanium dioxide with a 33% aqueous solution of 1,2-diaminopropane (DAP) under solvothermal conditions leads to the formation of colourless octahedral crystals of the novel germanate (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2 H₂O. The compound crystallises in the orthorhombic space group *Pbca*, *a* = 14.4155(10), *b* = 12.9384(9), *c* = 14.5417(8) Å, *V* = 2712.2 (3) Å³; *Z* = 4. The structure consists of an anionic [Ge₉(OH)₄O₁₈]^{4−} framework with isolated [1,2-DAPH₂]²⁺ cations and water molecules in the channels of the structure. The primary building units of the anionic framework are GeO₄ tetrahedra, GeO₅ trigonal bipyramids, and GeO₆ octahedra. The asymmetric unit consists of two GeO₅ units sharing a common edge to form a Ge₂O₈ unit. This Ge₂O₈ unit is corner-linked to two GeO₄ tetrahedra, and finally one GeO₄ tetrahedron is connected to a GeO₆ octahedron by corner-sharing. The connectivity yields a chain-like Ge₅O₁₉ fragment as a secondary building unit (SBU). The chain fragments are interconnected with each other forming the three-dimensional framework. Three types of channels with diameters ranging from 5.98 to 8.025 Å intersect the three-dimensional germanate network. Upon heating the compound decomposes in three steps starting at about 125 °C losing the water and the 1,2-diaminopropane molecules.

In situ X-ray diffraction experiments show that the water molecules are removed retaining the integrity of the skeleton of the material. The removal of H₂O is accompanied with an anisotropic shrinkage of the structure. The original lattice parameters were obtained after the uptake of water.

Key words: Germanate, Hydrothermal Synthesis, Thermal Stability

Introduction

The preparation of porous materials using the solvothermal route is a fast growing area of inorganic solid state chemistry. The most well-known materials are zeolites exhibiting channels and pores defined by corner sharing TO₄ tetrahedra (T = Si, Al). Zeolites have been extensively studied because of their interesting properties and their application in industrial processes as catalysts and ion exchangers. The wide range of possible applications of microporous materials is the reason why the research and preparation of related microporous crystalline materials are highly attractive. Recently, a number of aluminosilicates and gallophosphates and metal sulphides with organic amines or quaternary ammonium ions as template molecules have been synthesised and received considerable attention [1–6].

Germanates are of particular interest because their frameworks may be formed from several primary building units, *i.e.* the GeO₄ tetrahedron, the GeO₆ octahedron and the GeO₅ trigonal bipyramid [7–19]. A systematic variation of the preparation conditions should yield new germanate frameworks formed by the interconnection of the aforementioned primary building units. Interestingly, there are only a small number of germanates reported until now which were prepared via solvothermal syntheses [7–19].

Here we report on the synthesis, crystal structure and thermal stability of the new germanate with composition (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2 H₂O.

Experimental Section

Synthesis

The title compound was synthesised under solvothermal conditions from GeO₂ (0.523 g, 5 mmol) and 9 ml of a 33%

Table 1. Selected distances [Å] and angles [°] for (1,2-DAP)₂Ge₉(OH)₄O₁₈ · 2H₂O. Estimated standard deviations are given in parentheses.

Ge(1)—O(1) 2×	1.870(3)	Ge(1)—O(8) 2×	1.904(3)
Ge(1)—O(11) 2×	1.873(3)	Ge(2)—O(1)	1.740(3)
Ge(2)—O(2)	1.754(3)	Ge(2)—O(3)	1.766(3)
Ge(2)—O(4)	1.718(3)	Ge(3)—O(4)	1.820(3)
Ge(3)—O(5)	1.790(3)	Ge(3)—O(6)	1.776(3)
Ge(3)—O(7)	1.800(3)	Ge(3)—O(8)	1.962(3)
Ge(4)—O(2)	1.779(3)	Ge(4)—O(7)	1.792(3)
Ge(4)—O(8)	1.986(3)	Ge(4)—O(9)	1.771(3)
Ge(4)—O(10)	1.828(3)	Ge(5)—O(3)	1.768(3)
Ge(5)—O(5)	1.755(3)	Ge(5)—O(10)	1.721(3)
Ge(5)—O(11)	1.733(3)		
O(1)—Ge(1)—O(8)	90.91(12)	O(1)—Ge(1)—O(11)	90.85(12)
O(1)—Ge(1)—O(8)	89.09(12)	O(1)—Ge(1)—O(11)	89.15(12)
O(11)—Ge(1)—O(8)	90.36(12)	O(11)—Ge(1)—O(8)	89.64(12)
O(1)—Ge(2)—O(2)	111.65(14)	O(1)—Ge(2)—O(3)	110.77(13)
O(2)—Ge(2)—O(3)	108.54(15)	O(4)—Ge(2)—O(1)	103.65(14)
O(4)—Ge(2)—O(2)	110.48(14)	O(4)—Ge(2)—O(3)	111.73(14)
O(4)—Ge(3)—O(8)	167.81(12)	O(5)—Ge(3)—O(4)	91.44(13)
O(5)—Ge(3)—O(7)	119.47(16)	O(5)—Ge(3)—O(8)	92.69(13)
O(6)—Ge(3)—O(4)	94.98(14)	O(6)—Ge(3)—O(5)	113.64(16)
O(6)—Ge(3)—O(7)	126.62(15)	O(6)—Ge(3)—O(8)	93.86(14)
O(7)—Ge(3)—O(4)	88.87(13)	O(7)—Ge(3)—O(8)	79.12(12)
O(2)—Ge(4)—O(7)	118.17(15)	O(2)—Ge(4)—O(8)	91.85(13)
O(2)—Ge(4)—O(10)	90.10(13)	O(7)—Ge(4)—O(8)	78.67(12)
O(7)—Ge(4)—O(10)	91.10(13)	O(9)—Ge(4)—O(2)	115.91(17)
O(9)—Ge(4)—O(7)	125.49(17)	O(9)—Ge(4)—O(8)	93.51(14)
O(9)—Ge(4)—O(10)	95.13(15)	O(10)—Ge(4)—O(8)	169.26(13)
O(5)—Ge(5)—O(3)	109.80(15)	O(10)—Ge(5)—O(3)	108.55(15)
O(10)—Ge(5)—O(5)	113.13(15)	O(10)—Ge(5)—O(11)	102.84(14)
O(11)—Ge(5)—O(3)	110.75(14)	O(11)—Ge(5)—O(5)	111.59(15)

Table 2. Technical details of data acquisition and selected refinement results for (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2H₂O.

Empirical formula	(1,2-DAPH ₂) ₂ Ge ₉ (OH) ₄ O ₁₈ · 2H ₂ O
Colour, -habit	colourless octahedral crystals
Crystal size	0.08 × 0.08 × 0.08 mm
Molecular weight	1197.96 g/mol
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Calculated density	2.933 g/cm ³
<i>a</i>	14.4155(10) Å
<i>b</i>	12.9384(9) Å
<i>c</i>	14.5417(8) Å
<i>V</i>	2712.2(3) Å ³
<i>Z</i>	4
Temperature	293 K
Scan range	5° ≤ 2θ ≤ 54° −1 ≤ <i>h</i> ≤ 18 −16 ≤ <i>k</i> ≤ 16 −18 ≤ <i>l</i> ≤ 1
Measured reflections	7395
Independent reflections	2949
Reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	2320
<i>μ</i>	9.91 mm ^{−1}
<i>R</i> _{int}	0.0394
Absorption correction	face-indexed
Min./max. trans.	0.2107/0.2817
<i>R</i> 1 (<i>F</i> _o > 4σ(<i>F</i> _o))	0.0285
<i>R</i> 1 (all reflections)	0.0473
<i>wR</i> 2 (<i>F</i> _o > 4σ(<i>F</i> _o))	0.0663
<i>wR</i> 2 (all reflections)	0.0701
Δρ	−0.93/0.70 e/Å ³
Goodness of fit	1.131

aqueous solution of 1,2-diaminopropane. The pH value of the solution was 13.25. The mixture was heated to 160 °C for 7 days in a teflon-lined steel autoclave (*ca.* 30 ml). The homogeneous product consisting of colourless crystals with an octahedral shape was filtered off, washed with distilled water and dried on air. Typical dimensions of the crystals are 0.1 × 0.1 × 0.1 mm. (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2H₂O (1197.96) calcd. C 6.01, H 2.19, N 4.68; found C 5.8, H 2.7, N 4.42.

Structure determination

Intensities were collected on a Nonius CAD-4 diffractometer using monochromated Mo-K_α radiation (*λ* = 0.71073 Å). The intensities were corrected for Lorentz, polarisation and absorption effects. Structure solution was performed using SHELXS-97 [20]. Refinement was done against *F*² using SHELXL-97 [21]. All heavy atoms were refined anisotropically. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of data acquisition and refinement results are summarised in Table 2.

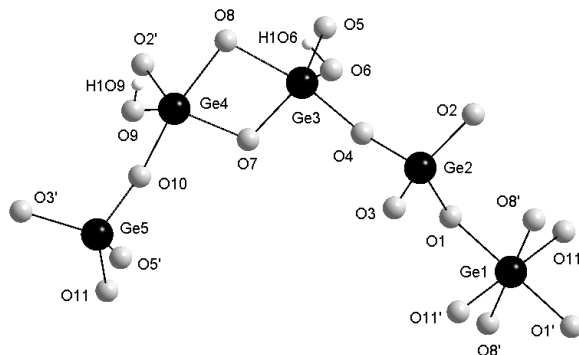


Fig. 1. The interconnection of the different GeO₄ polyhedra into a chain within the (011) plane. Atoms with superscripts are generated by symmetry operations.

X-ray powder diffractometry

The X-ray powder patterns were recorded on a STOE STADI P transmission powder diffractometer with a position sensitive detector (CuK_α-radiation *λ* = 1.540598 Å) in transmission geometry.

Thermoanalytical measurements

DTA-TG-MS measurements were performed simultaneously in Al₂O₃ crucibles under a dynamic helium or nitrogen atmosphere (flow rate 75 ml min⁻¹) using different heating rates with the STA-409CD thermobalance with Skimmer coupling from Netzsch, which is equipped with a quadrupole mass spectrometer QMA 400 from Balzers.

IR Spectroscopy

IR spectra were measured in the region from 500 to 4000 cm⁻¹ with a ATI-Mattson Genesis Infrared spectrometer with 2 cm⁻¹ resolution. The sample was dispersed in a KBr pellet.

Results and Discussion

Crystal structure

The title compound (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2 H₂O crystallises in the orthorhombic space group *Pbca* with four formula units in the unit cell. Selected interatomic distances are listed in Table 1. The description of the structure of the anionic framework is based on building units of different complexity that were also observed in other microporous germanates [7–19]. The asymmetric unit contains five crystallographically independent Ge atoms and eleven O atoms. The Ge atoms have three different coordination numbers and form the primary building units (Fig. 1).

The Ge(1) atom is coordinated by six O atoms to form a moderately distorted octahedron with Ge—O bond lengths ranging from 1.873(3) to 1.904(3) Å. These values are comparable to those found in the rutile type structure of GeO₂ (Ge—O: 1.868–1.911 Å) and in other germanates [7–11,14,22]. The Ge(2) and Ge(5) atoms are in a slightly distorted tetrahedral environment with Ge—O distances between 1.718(4) and 1.768(3) Å and O—Ge—O angles ranging from 103.7(2) to 111.7(2)°. The Ge—O distances are in the same range as reported for GeO₂ in the quartz modification (1.741 Å) and in other germanates [7–11, 14, 15, 23]. The remaining two Ge atoms are in a strongly distorted trigonal bipyramidal environment. The Ge—O bond lengths scatter from 1.771(3) to 1.986(3) Å. Three different types of oxygen atoms are observed. Most of the O atoms act as two coordinated bridging atoms (Ge—O: 1.718(3)–1.873(3) Å, Ge—O—Ge angles: 107.7(2)–134.8(2)°). The second type are terminal hydroxyl groups (O(6) and O(4)) with Ge—O distances of 1.771(3) and 1.776(3) Å. The third

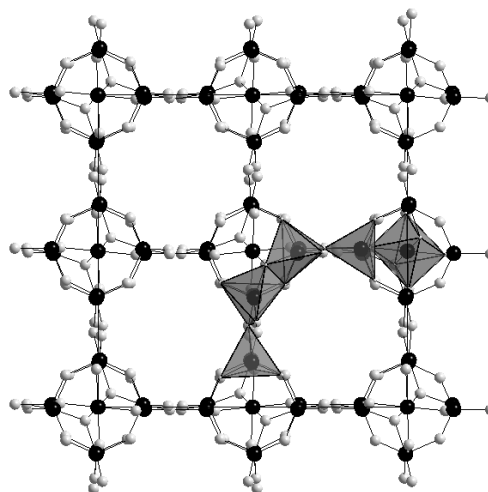


Fig. 2. The structure of the anionic Ge₉(OH)₄O₁₈ framework with view along the [010] direction (the [1,2-DAPH₂]²⁺ and water guest molecules are omitted for clarity).

type is the O(8) atom which connects three Ge atoms (Ge(1), Ge(3), Ge(4)) and exhibits the longest Ge—O distances (1.904(3) and 1.986 Å). The Ge—O—Ge angles scatter between 94.5(2) and 132.7(2)°. These values are in the same range as reported for other germanates [7–19].

The GeO_x polyhedra are linked to form a chain-like fragment within the (101) plane as the secondary building unit (SBU) (Fig. 1). The two trigonal bipyramids share a common edge (O(8) and O(7)) yielding a Ge₂O₈ unit. This unit is corner linked to two GeO₄ tetrahedra via O(4) and O(10). Finally, the Ge(1)O₆ octahedron shares a corner with the Ge(2)O₄ tetrahedron via O(1).

The interconnection of the SBU's yields a three-dimensional framework with three different kinds of channels. The smallest channel with a diameter of 5.98 Å (measured from coordinate to coordinate) is directed along the *b* axis and the aperture is composed of eight Ge atoms (Fig. 2). The second channel along [101] has a diameter of about 6.56 Å and the window is composed of ten Ge atoms (Fig. 3). The third type of channels with an opening of ten Ge atoms runs along $\bar{1}$ 01 and exhibits a diameter of 8.025 Å. The water and [1,2-DAPH₂]²⁺ cations are located within the channels and form hydrogen bonds to O atoms of the germanate framework.

The different channels are surrounded by Ge₉O₁₈ clusters which may be viewed as another secondary

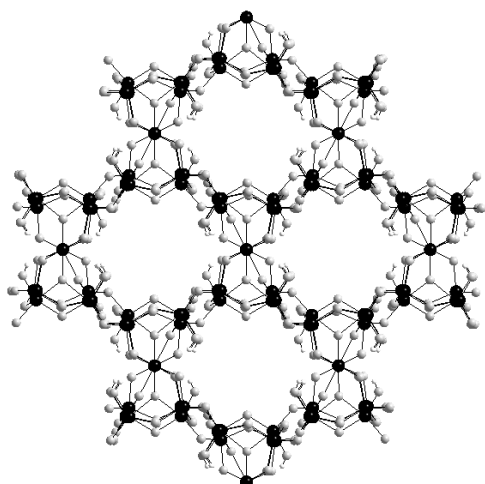


Fig. 3. The Ge₉(OH)₄O₁₈ framework with view along the [101] direction (the [1,2-DAPH₂]²⁺ and water guest molecules are omitted for clarity).

building unit. The cluster has a GeO₆ octahedron as the central unit and the eight Ge atoms at the corners of the cluster are in a tetrahedral coordination. We note that the Ge₉O₁₈ unit was also found in other germanates [7, 8, 11, 16]. For instance, in [Ge₁₈O₃₈(OH₄)] [C₂N₂H₁₀]₄ · 2H₂O, which has a different composition compared to the title compound, these units are interconnected to form a three-dimensional network with three types of channels exhibiting different sizes compared to those of the title compound. Two channels have the same ring aperture with an oval 10-membered window and one channel consisting of 8 Ge atoms [7]. In the IR spectrum of the title compound the absorption at 3420 cm⁻¹ is due to the stretching vibration of the OH groups while bands at 2940 and 2465 cm⁻¹ arise from N—H vibrations of the protonated 1,2-diaminopropane. The absorption of the Ge—O vibrations range from 785 to 515 cm⁻¹.

Thermal investigations

The thermal stability of the compound was investigated using simultaneous differential thermoanalysis (DTA) and thermogravimetry (TG) measurements under an N₂ atmosphere as well as simultaneous DTA-TG-MS measurements under a He atmosphere. The compound decomposes mainly in three steps with a total weight loss of 16.5%. The first weight loss of 2.9% occurs between 125 °C and 210 °C and is accompanied by an endothermic event at T_p = 191 °C.

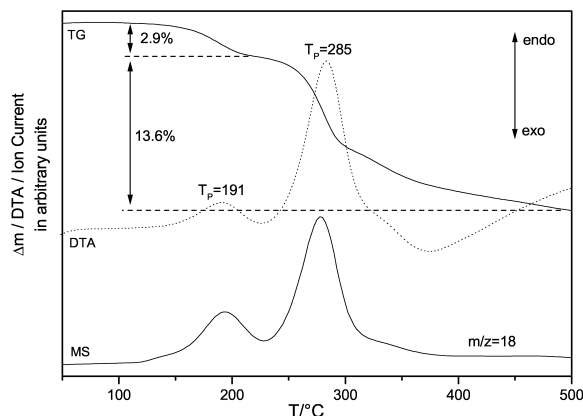


Fig. 4. DTA-TG-MS (trend scan) curves for (1,2-DAPH₂)₂Ge₉(OH)₄O₁₈ · 2 H₂O; (*m/z* = 18 (H₂O and fragment of the exhausted amine), T_p = peak temperature).

The mass change corresponds to the emission of H₂O (calculated 3%). This interpretation is supported by the MS measurements showing the signal of H₂O (*m/z* = 18) (Fig. 4). During the next two steps (210–500 °C) the two [1,2-DAPH₂]²⁺ cations are emitted ($\Delta m_{\text{exp}} = 13.6\%$, $\Delta m_{\text{calc}} = 12.7\%$). The decomposition is accompanied by an endothermic event at T_p = 285 °C. In the X-ray powder pattern of the decomposition product crystalline GeO₂ could be identified.

In further experiments the heating process was stopped at 210 °C after the loss of water. The X-ray powder pattern of the initial material is dominated by three strong reflections between 11 and 14° 2 θ (2 θ /(hkl): 11.045 (111), 12.227 (002)/(200) and 13.728 (020)). In the pattern of the dehydrated phase the three reflections are shifted to larger 2 θ values indicative of a shrinkage of the structure (Fig. 5). The lattice parameters obtained applying a least-squares refinement are *a* = 14.12(1), *b* = 12.265(5), *c* = 14.639(6) Å, *V* = 2535.1(4) Å³. All reflections in the powder pattern of the dehydrated phase can be indexed assuming space group *Pbca* and the lattice parameter refinement yields FOM(30) = 54.3 (0.010, 53). Comparing these values with those of the starting material the anisotropy of the contraction is obvious. For the *a*- and *b*-axis a contraction of about 2.1% and 5.5% is observed, respectively, whereas the *c*-axis is slightly expanded. The overall change of the unit cell volume amounts to 7%.

The loss of water is reversible and upon storing the dehydrated product in a wet atmosphere water is incorporated again. The X-ray powder pattern after water re-

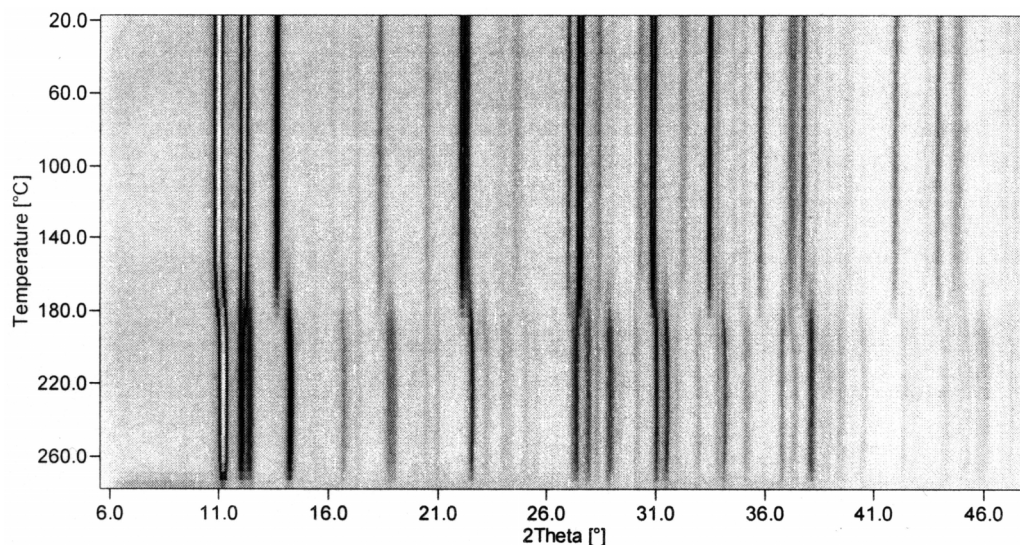


Fig. 5. Temperature resolved X-ray powder patterns of (1,2-DAPH₂)₂ Ge₉(OH)₄O₁₈ · 2 H₂O.

intercalation is identical with that of the genuine starting compound.

Supplementary Data

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-

185044. 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).

Acknowledgements

We gratefully acknowledge the financial support by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (DFG).

- [1] D.A. Bruce, A.P. Wilkinson, M.G. White, J.A. Bertrand, *J. Solid State Chem.* **125**, 228 (1996).
- [2] P. Feng, X. Bu, G.D. Stucky, *Nature* **388**, 735 (1997).
- [3] M. Estermann, L.B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* **352**, 320 (1991).
- [4] M.P. Attfield, R.E. Morris, E. Gutiérrez-Puebla, A. Monge-Bravo, A.K. Cheetham, *J. Chem. Soc., Chem. Commun.* 843 (1995).
- [5] C.L. Cahill, B. Gugliotta, J.B. Parise, *Chem. Commun.* 1715 (1998).
- [6] C.L. Cahill, J.B. Parise, *J. Chem. Soc., Dalton Trans.* 1475 (2000).
- [7] R.H. Jones, J. Chen, J.M. Thomas, A. George, M.B. Hursthouse, R. Xu, S. Li, Y. Lu, G. Yang, *Chem. Mater.* **4**, 808 (1992).
- [8] K. Sun, M.S. Dadachov, T. Conradsson, X. Zou, *Acta Crystallogr.* **C56**, 1092 (2000).
- [9] C. Cascales, E. Gutiérrez-Puebla, M.A. Monge, C. Ruiz-Valero, *Angew. Chem.* **110**, 135 (1998); *Angew. Chem. Int. Ed.* **37**, 129 (1998).
- [10] C. Cascales, E. Gutiérrez-Puebla, M.A. Monge, M. Iglesias, C. Ruiz-Valero, *Angew. Chem.* **111**, 2592 (1999); *Angew. Chem. Int. Ed.* **38**, 2436 (1999).
- [11] H. Li, M. Eddaoudi, O.M. Yaghi, *Angew. Chem.* **111**, 682 (1999); *Angew. Chem. Int. Ed.* **38**, 653 (1999).
- [12] H. Li, O.M. Yaghi, *J. Am. Chem. Soc.* **120**, 10569 (1998).
- [13] X. Bu, P. Feng, G.D. Stucky, *J. Am. Chem. Soc.* **120**, 11204 (1998).
- [14] Y. Zhou, H. Zhu, Z. Chen, M. Chen, Y. Xu, H. Zhang, D. Zhao, *Angew. Chem.* **113**, 2224 (2001); *Angew. Chem. Int. Ed.* **40**, 2166 (2001).
- [15] C. Cascales, E. Gutiérrez-Puebla, M. Iglesias, M.A. Monge, M. Iglesias, C. Ruiz-Valero, N. Snejko, *Chem. Commun.* 2145 (2000).
- [16] X. Bu, P. Feng, G.D. Stucky, *Chem. Mater.* **12**, 1505 (2000).
- [17] J. Plévert, T.M. Gentz, A. Laine, H. Li, V.G. Young, O.M. Yaghi, M.J. O'Keeffe, *J. Am. Chem. Soc.* **123**, 12706 (2001).

- [18] L. Beitone, T. Loiseau, G. Ferey, *Inorg. Chem.* **41**, 3962 (2002).
- [19] A. Tripathi, V. G. Young, G. M. Johnson, C. L. Cahill, J. B. Parise, *Acta Crystallogr.* **C55**, 496 (2000).
- [20] G. M. Sheldrick, SHELXS-97. Program for the solution of crystal structures, University of Göttingen, Germany (1997).
- [21] G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, University of Göttingen, Germany (1997).
- [22] W. H. Bauer, A. A. Khan, *Acta Crystallogr.* **B27**, 2133 (1971).
- [23] G. S. Smith, P. B. Isaacs, *Acta Crystallogr.* **17**, 842 (1964).