[6] a) P. Stilbs, M. E. Moseley, *J. Chem. Soc. Faraday Trans. 2* **76** (1980) 729; b) P. Stilbs, *J. Magn. Reson.* **58** (1984) 152; c) J. Hennig, H.-H. Limbach, *J. Am. Chem. Soc.* **106** (1984) 869.

[7] a) M. J. Crosswell, M. M. Harding, S. Sternhell, *J. Am. Chem. Soc.* **108** (1986) 3608; b) M. J. Crosswell, L. D. Field, M. M. Harding, S. Sternhell, *ibid.* **109** (1987) 2335.

[8] a) H.-H. Limbach, J. Hennig, R. D. Kendrick, C. S. Yannoni, *J. Am. Chem. Soc.* **106** (1984) 4059; b) H.-H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick, C. S. Yannoni, *ibid.* **109** (1987) 929; c) *Angew. Chem.* **99** (1987) 241; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 247; d) B. Wehrle, H.-H. Limbach, M. Köcher, O. Ermer, E. Vogel, *ibid.* **99** (1987) 914 and **26** (1987) 934; e) B. Wehrle, H. Zimmermann, H.-H. Limbach, *Ber. Bunsenges. Phys. Chem.* **91** (1987) 941; f) H.-H. Limbach, B. Wehrle, M. Schlabach, R. D. Kendrick, C. S. Yannoni, *J. Magn. Reson.* **77** (1988) 84; g) L. Frydman, A. C. Olivieri, L. E. Diaz, B. Frydman, F. G. Morin, C. L. Mayne, D. M. Grant, A. D. Adler, *J. Am. Chem. Soc.* **110** (1988) 336; h) L. Frydman, A. C. Olivieri, L. E. Diaz, A. Valasinas, B. Frydman, *ibid.* **110** (1988) 5651.

[9] a) S. Völker, J. H. van der Waals, *Mol. Phys.* **32** (1976) 1703; b) S. Voelker, R. Macfarlane, *IBM Res. Dev.* **23** (1979) 547.

[10] a) J. Almlöf, *Int. J. Quantum Chem.* **8** (1974) 915; b) H.-H. Limbach, J. Hennig, *J. Chem. Phys.* **71** (1979) 3120; c) H.-H. Limbach, J. Hennig, J. Stulz, *ibid.* **78** (1983) 5432; d) H.-H. Limbach, *ibid.* **80** (1984) 5343; e) V. A. Kusmitsky, K. N. Solovyov, *J. Mol. Struct.* **65** (1980) 219; f) A. Sarai, *J. Chem. Phys.* **76** (1982) 5554; g) *ibid.* **80** (1984) 5431; h) G. I. Bersuker, V. Z. Polinger, *Chem. Phys.* **86** (1984) 57; i) K. M. Merz, C. H. Reynolds, *J. Chem. Soc. Chem. Commun. 1988,* 90; j) Z. Smedarchina, W. Siebrand, T. A. Wildman, *Chem. Phys. Lett.* **143** (1988) 395; k) D. C. Rawlings, E. R. Davidson, M. Gouterman, *Theor. Chim. Acta* **61** (1982) 227.

[11] H. W. Whitlock, R. Hanover, M. Y. Oester, B. K. Bower, *J. Am. Chem. Soc.* **91** (1969) 7485.

[12] C. K. Chang, *Biochemistry* **19** (1980) 1971.

[13] H. Scheer, J. J. Katz in K. M. Smith (Ed.): *Porphyrins and Metalloporphyrins,* Elsevier, Amsterdam 1975, p. 440ff.

[14] a) Y. Harel, J. Manassen, *J. Am. Chem. Soc.* **100** (1978) 6228; b) A. M. Stolzenberg, M. T. Stershic, *Magn. Reson. Chem.* **25** (1987) 256; c) Y. Harel, J. Manassen, *Org. Magn. Reson.* **16** (1981) 290; d) A. M. Stolzenberg, L. O. Spreer, R. H. Holm, *J. Am. Chem. Soc.* **102** (1980) 364; e) R. Thomas, *Dissertation,* Braunschweig 1967; f) W. Hoppe, G. Will, J. Gassmann, H. Weichselgartner, *Z. Kristallogr.* **128** (1969) 18.

[15] W. B. T. Cruse, P. J. Harrison, O. Kennard, *J. Am. Chem. Soc.* **104** (1982) 2376.

[16] K. M. Barkigia, J. Fajer, C. K. Chang, G. J. B. Williams, *J. Am. Chem. Soc.* **104** (1982) 315.

[17] K. M. Barkigia, J. Fajer, L. D. Spaulding, G. J. B. Williams, *J. Am. Chem. Soc.* **103** (1981) 176.

[18] F. A. Burkhalter, E. C. Meister, U. Wild, *J. Phys. Chem.* **91** (1987) 3228.

[19] a) K. M. Smith, D. A. Goff, R. J. Abraham, J. E. Plant, *Org. Magn. Reson.* **21** (1983) 505; b) R. J. Abraham, K. M. Smith, *J. Am. Chem. Soc.* **105** (1983) 5737.

[20] J. D. Keegan, A. M. Stolzenberg, Y. C. Lu, R. E. Linder, G. Barth, A. Moscowitz, E. Bunnenberg, C. Djerassi, *J. Am. Chem. Soc.* **104** (1982) 4305.

[21] S. Voelker, R. M. Macfarlane, *J. Chem. Phys.* **73** (1980) 4478.

[22] L. W. Johnson, M. D. Murphy, C. Pope, M. Foresti, J. R. Lombardi, *J. Chem. Phys.* **86** (1987) 4335.

[23] TPC (= 5,10,15,20-tetraphenyl[^{15}N$_4$]chlorin = 5,10,15,20-tetraphenyl-[^{15}N$_4$]-7,8-dihydroporphyrin) was prepared, in a similar way as described in [11] for the unlabeled material, from TPP (= 5,10,15,20-tetraphenyl[^{15}N$_4$]porphyrin); TPP was prepared according to [26], [^{15}N]pyrrole synthesized as described in [8d]. Note that the name 5,10,15,20-tetraphenyl[^{15}N$_4$]-2,3-dihydroporphyrin proposed in the IUPAC recommentations [27] is not consistent with the findings of this study. The ^{15}N labeling of all compounds in this study was performed in order to obtain reliable results which are not affected by intermolecular proton exchange and ^{14}N quadrupole relaxation.

[24] TPBc (= 5,10,15,20-tetraphenyl[^{15}N$_4$]bacteriochlorin) was prepared, in a way similar to that described in [11] for the unlabeled material, from TPP.

[25] TPiBc (= 5,10,15,20-tetraphenyl[^{15}N$_4$]isobacteriochlorin) was prepared, in a way similar to that described in [11] for the unlabeled material, from TPP.

[26] F. R. Longo, E. J. Thorne, A. D. Adler, S. Dym, *J. Heterocycl. Chem.* **12** (1975) 1305.

[27] G. P. Moss, *Pure Appl. Chem.* **59** (1987) 779.

[28] R. J. Abraham, C. J. Medforth, K. M. Smith, D. A. Goff, D. J. Simpson, *J. Am. Chem. Soc.* **109** (1987) 4786.

[29] G. Otting, H. Rumpel, L. Meschede, G. Scherer, H.-H. Limbach, *Ber. Bunsenges. Phys. Chem.* **90** (1986) 1122.

[30] Intermolecular proton transfer would lead to breakdown of the ^{1}H-^{15}N splitting pattern [29].

[31] The activation parameters were obtained from a total of 16 spectra of TPC in C$_2$D$_2$Cl$_4$ and [D$_8$]toluene in the temperature range 298 to 406 K; no solvent effects were observed.

[32] In monodeuterated TPiBc, these signals are sharp at −100°C due to a kinetic HH/HD isotope effect which indicates that the broadening in the bottom spectrum of Figure 3 stems from proton transfer and not from slow rotational diffusion [6].

[33] We tentatively assign the signal at $\delta = 4.6$ to H-21 and the signal at $\delta = 6.1$ to H-23. For the atomic numbering scheme see legend to Figure 1.

[34] $k_{AC \to DB}$ was obtained from 7 spectra between 170 and 280 K, $k_{AC \to BD}$ from 4 spectra between 270 and 320 K. Note that the line shape of the outer proton signals, which are not shown here, is sensitive only to the process AC→DB and not to the process AC→BD.

Selective Molecular Recognition of Trihydroxybenzenes**
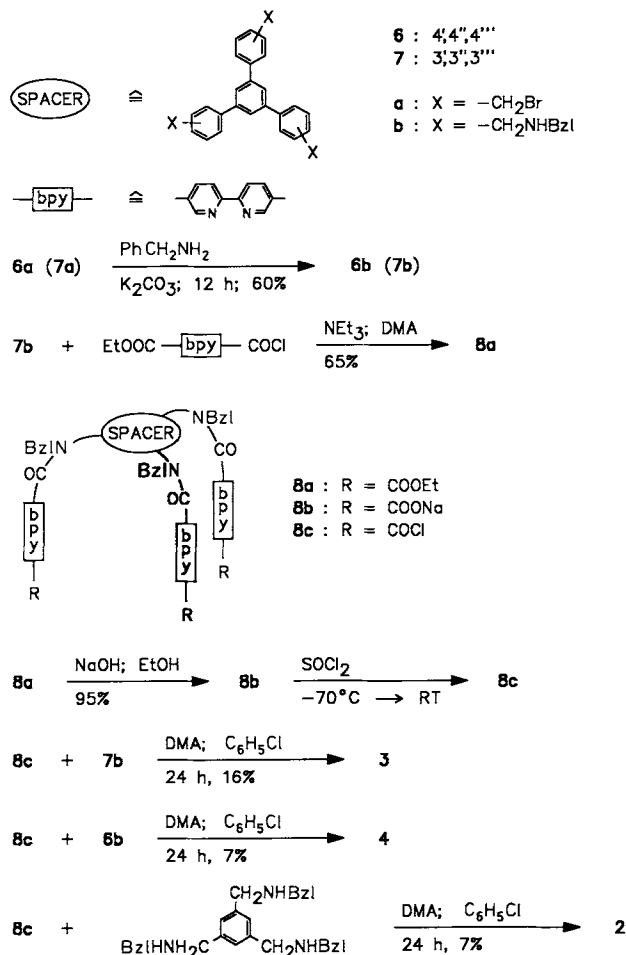
By *Frank Ebmeyer* and *Fritz Vögtle**

The complexation of organic molecules in nonaqueous media is currently being intensively investigated.[1] We report here on the synthesis and complexation properties of the macrobicyclic compounds **2-4**,[2] which exhibit a remarkable selectivity for phenolic substrates, in particular trihydroxybenzenes. Although the bipyridine ligand **1**, synthesized in 1986, strongly complexes small metal cations,[3] it does not bind organic molecules. The successive expansion of the host cavity with the C_3-symmetric spacers introduced by us[4] leads to the new complex-forming molecules **2-4** having larger cavities.

1   2   3

4   5

R = Benzyl
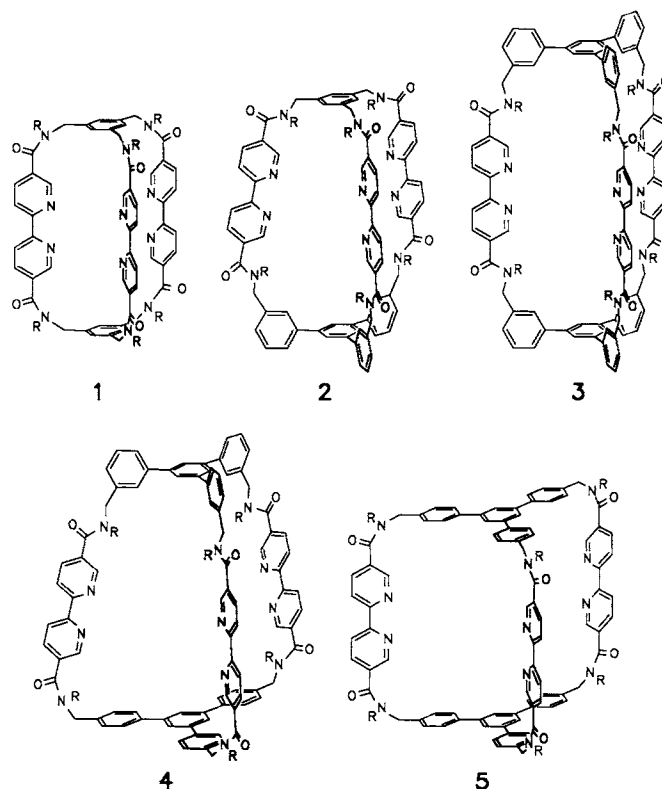
[*] Prof. Dr. F. Vögtle, Dipl.-Chem. F. Ebmeyer
Institut für Organische Chemie und Biochemie der Universität
Gerhard-Domagk-Strasse 1, D-5300 Bonn 1 (FRG)

Attempted transfer of the reaction conditions used in the cyclization to **1**[3] to the expanded tris(bipyridine) compound **5** (containing the 4',4'',4'''-triphenylbenzene spacer) was unsuccessful. Only upon employing the *meta*-substituted spacer—under modified conditions[5]—was the large-cavity compound **3** obtained in 16% yield.[6] The macrobicyclic compounds **2** and **4** with conical cavities[8] were obtained similarly, in yields of 7% each (Scheme 1).

2–4. The complexation of the phenolic guests is selective. As shown in Table 1, only certain trihydroxybenzenes are complexed, but not structurally related compounds or the isomer pyrogallol (1,2,3-trihydroxybenzene). These findings reflect a marked guest selectivity found earlier in other studies.[11]

Table 1. Host/guest selectivities (+, complexation; −, no complexation). Host concentrations ca. 2×10^{-3} mol L^{-1}; solvent CD_2Cl_2, 25 °C.

Guest	2	3	4
(3,5-dihydroxy / catechol derivatives)	+	+	−
(acetyl / aldehyde trihydroxy derivatives)	+	+	+
(carboxyl trihydroxy / resorcinol derivatives)	−	−	−
(dicarboxylic ammonium / tris(aminomethyl) derivatives)	−	−	−

Scheme 1. Bzl = benzyl, DMA = dimethylacetamide.

6 : 4',4'',4'''
7 : 3',3'',3'''

a : X = −CH₂Br
b : X = −CH₂NHBzl

6a (7a) → **6b (7b)**   PhCH₂NH₂ / K₂CO₃; 12 h; 60%

7b + EtOOC—bpy—COCl → **8a**   NEt₃; DMA / 65%

8a : R = COOEt
8b : R = COONa
8c : R = COCl

8a → **8b**   NaOH; EtOH / 95%
8b → **8c**   SOCl₂ / −70 °C → RT

8c + **7b** → **3**   DMA; C₆H₅Cl / 24 h, 16%
8c + **6b** → **4**   DMA; C₆H₅Cl / 24 h, 7%
8c + BzlHNH₂C—(CH₂NHBzl)(CH₂NHBzl) → **2**   DMA; C₆H₅Cl / 24 h, 7%

The new ligands, hexadentate in the cavity,[9] are tailor-made for incorporating complementary trifunctional guest molecules. However, attempts to form inclusion complexes with tricarboxylic acids such as 1,3,5-benzenetricarboxylic acid or the tris(ammonium) salt of 1,3,5-tris(aminomethyl)benzene as guests (dichloromethane as solvent) were unsuccessful. On the other hand, several trihydroxybenzenes were complexed. The guest substances, which are insoluble in dichloromethane, dissolved after addition of the host compounds **2–4**; the ¹H NMR spectra of the filtered solutions display signals of host *and* guest molecules. The simple pattern of the guest signals—not split in the 400 MHz spectrum—indicates a symmetrical complexation.[10]

Integration of the NMR absorptions reveals a 1:1 stoichiometry of the host–guest complexes, even when starting with nonstoichiometric ratios of host and guest molecules. A 1:3 stoichiometry was found for the guests picric acid (2,4,6-trinitrophenol) and nitrophloroglucinol (1,3,5-trihydroxynitrobenzene), which do not fit into the cavities of

Selectivity is also observed upon varying the host compounds: whereas neither the host **1** nor its open-chain precursor **8a** complexes phloroglucinol and 1,2,4-trihydroxybenzene, these compounds are indeed complexed by **2** and **3** (but not by the isomer **4**). This finding supports the notion of hydrogen bonding between host and guest in a suitably sized cavity. In agreement with this, the hosts **2**, **3**, and **4** also discriminate between phloroglucinol derivatives: even a small structural change such as the introduction of a methyl or a carboxyl group results in loss of complexation.

A gravimetric method[12] revealed an appreciable association constant of $11\,000 \pm 2000$ (in dichloromethane) for
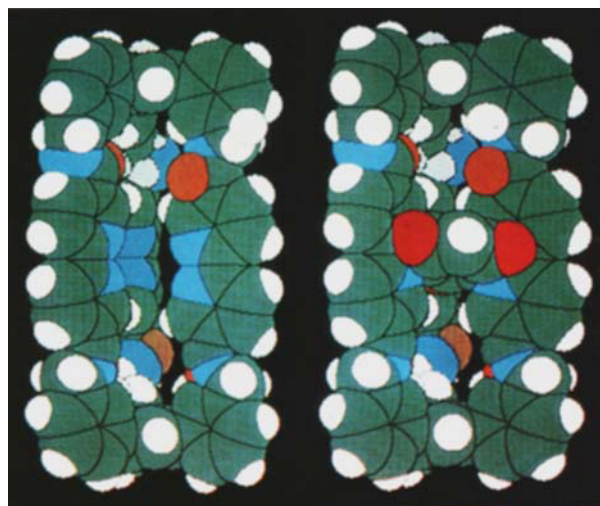

Fig. 1. Left: Host molecule **3** with empty cavity. Right: Space-filling model of the phloroglucinol complex of **3**; the phloroglucinol guest molecule lies perpendicular to the plane of the page between the three bipyridine units of the host **3** [16].

0570-0833/89/0101-0080 $ 02.50/0

the complex of **3** with phloroglucinol; this high value can be explained by the formation of multiple hydrogen bonds between host and guest in the cavity. The exact fitting of the guest into the interior of the "receptor molecules" **2–4** is supported not only by the marked host/guest selectivities and the high association constants, but also by the fact that irradiation of the resonance of the bipyridine protons results in a small but significant NOE effect (-0.5%) for the guest protons.

Compounds **1–4** illustrate that the cavity of host compounds can be changed selectively with respect to size and shape by variation of the spacer, allowing the direct synthesis of selective complex-forming molecules.[13] The conical shape of the cavity, the high selectivity in the molecular recognition of trihydroxybenzenes, and the stabilization of phenolic guests toward oxidants[14] have hardly been achieved so far in a synthetic "receptor molecule".[15]

[1] a) Reviews: F. Diederich, *Angew. Chem. 100* (1988) 372; *Angew. Chem. Int. Ed. Engl. 27* (1988) 362; cf. also J.-M. Lehn, *ibid. 100* (1988) 91 and *27* (1988) 89; b) R. E. Sheridan, H. W. Whitlock, Jr., *J. Am. Chem. Soc. 110* (1988) 4071.

[2] Host compounds of this type belong neither to the crowns and cryptands nor to the spherands, hemispherands, cryptophanes, or cavitands.

[3] a) S. Grammenudi, F. Vögtle, *Angew. Chem. 98* (1986) 1119; *Angew. Chem. Int. Ed. Engl. 25* (1986) 1122; b) S. Grammenudi, M. Franke, F. Vögtle, E. Steckhan, *J. Inclusion Phenom. 5* (1987) 695. c) Photophysics of the 1-Ru²⊕ complex: L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. v. Zelewsky, F. Vögtle, F. Ebmeyer, *J. Am. Chem. Soc. 110* (1988) 7210.

[4] P. Stutte, W. Kiggen, F. Vögtle, *Tetrahedron 43* (1987) 2065; cf. T. Merz, H. Wirtz, F. Vögtle, *Angew. Chem. 98* (1986) 549; *Angew. Chem. Int. Ed. Engl. 25* (1986) 567.

[5] The higher the dilution, the greater the amount of dimethylacetamide (DMA) in the solvent mixture; different eluent for chromatography, cf. [6].

[6] a) *Experimental procedure* for **3**: Solutions of the acid chloride **8c** (4.34 g, 3.10 mmol) in 250 mL of DMA (Fluka, puriss.) and the triamine **7b** (4.11 g, 6.20 mmol) in 250 mL of dry chlorobenzene were simultaneously added dropwise under argon over 12 h to a mixture of chlorobenzene (750 mL) and DMA (250 mL) at room temperature [7]. The reaction mixture was then stirred for an additional 12 h and the resulting precipitate was filtered off. The red solution was concentrated and the residue was carefully dried under vacuum. Dichloromethane was then added to form a slurry, which was transferred to a silica gel column and chromatographed (eluent, dichloromethane/methanol 20 : 1), affording 1.00 g of **3** (16% yield, $R_F = 0.28$). b) All new macrocyclic compounds gave suitable elemental analyses, FAB mass spectra, and ¹H and ¹³C NMR spectra and exhibited the following R_F values (eluent: dichloromethane/methanol 20 : 1): 0.20 (**2**), 0.28 (**3**), 0.28 (**4**).

[7] Synthesis of the precursors: a) F. Vögtle, N. Sendhoff, *Chem. Ber. 121* (1988), in press; b) N. Sendhoff, *Dissertation*, Universität Bonn 1988; c) cf. [3b].

[8] Compare with the conical cavities of cyclodextrins and some macrotetracyclic hexalactams: F. Vögtle, B. Dung, *J. Inclusion Phenom. 6* (1988) 429.

[9] The pyridine rings in **2–5** freely rotate around their long axis according to the NMR findings; in the free ligands, some of the pyridine nitrogen atoms are presumably directed outwards—in analogy to the situation for crown ethers and cryptands.

[10] We consider a rapid exchange to be unlikely in view of the size of the host molecule and the multiple bonding sites. Compare the three-dimensional bonding and the similarly high complexation constants of cryptands toward ions.

[11] a) F. Vögtle, W. M. Müller, U. Werner, H.-W. Losensky, *Angew. Chem. 99* (1987) 930; *Angew. Chem. Int. Ed. Engl. 26* (1987) 901; b) cf. [1b].

[12] a) F. Diederich, K. Dick, *J. Am. Chem. Soc. 106* (1984) 8024; b) T. W. Bell, J. Liu, *ibid. 110* (1988) 3673.

[13] The ligands **2–4** can also be used to complex transition metals. We thank Prof. *A. von Zelewsky*, Fribourg, and Prof. *V. Balzani*, Bologna, for fruitful discussions.

[14] Solutions of phloroglucinol and **3** in dichloromethane do not turn dark upon daylong exposure to light and air, as is the case for aqueous solutions without host (the trihydroxybenzenes are only sparingly soluble in CD₂Cl₂ without addition of host).

[15] Cf. also: D. Heyer, J.-M. Lehn, *Tetrahedron Lett. 27* (1986) 5869; T. Fujita, J.-M. Lehn, *ibid. 29* (1988) 1709.

[16] The two pictures in Figure 1 were drawn with the "Atom 87" program, Oxford University Press, Beta-test version, October 1987.

A Silicogermanate with a Si : Ge Ratio ≥ 2 —an MFI Zeolite of Novel Composition**

By *Zelimir Gabelica** and *Jean-Louis Guth*

The pore volume, acidity and sorptive properties of zeolites can be modified and controlled by substitution of the framework atoms. We report herein results dealing with the substitution of Si by Ge in pure Si-bearing zeolites. A series of crystalline, microporous solids containing Si and Ge in an MFI type tetrahedral framework have been synthesized under hydrothermal conditions in the presence of $Pr_4N^{\oplus}$ ions as structure directing agents, over the whole pH range in the absence of alkali metal or ammonium cations. The unit cell composition of these solids, after removal of included organics, is $Si_{96-x}Ge_xO_{192}$, where $x \leq 34 \pm 4$. It is concluded that such a framework is built up from the 5-1 secondary building units (SBU) in which at least two tetrahedral centers are occupied by Ge. Such a high degree of substitution of Si by another tetravalent element has, until now, not been observed for an MFI type structure. Our method opens new pathways for preparing other highly substituted zeolites.

Both amorphous (glasses) and crystalline solid solutions are known in the binary system SiO_2–GeO_2.[1–2] In contrast to the open zeolitic structures, these phases, which were obtained at high temperature ($>700\,°C$), are not microporous. The frameworks of the natural zeolites[3] and of most of the synthetic molecular sieves[4] contain Si and Al atoms in the tetrahedral positions. Framework substitution by other tetravalent and trivalent elements is also well-known.[4] Recently, a series of zeolite structures containing only Si were reported.[5, 6] In the case of Si-MFI, the incorporation of $Ti^{4\oplus}$ in the framework has been reported but the degree of substitution was very low (ca. 2.5 wt.%).[7] Substitution of Si by Ge was, until now, not reported; clearly, this could only be achieved when a trivalent element (e.g., $Al^{3\oplus}$) was present in the framework.

The novel (Si,Ge)-MFI zeolites are obtained by heating an aqueous solution of the Si and Ge reactants at 60–220°C in the presence of a structure directing agent such as $Pr_4N^{\oplus}$. The crystallization time depends markedly on temperature, pH and the presence of fluoride ions. Typically, a mixture having the molar composition $GeCl_4$–SiO_2–HF–$0.5\,Pr_4NBr$–$8\,CH_3NH_2$–$35\,H_2O$ is heated in the presence of MFI seeds for 15 h at 180°C in PTFE coated autoclaves. The resulting solid, as identified by X-ray diffraction, has an MFI type structure. The unit cell composition, after calcination in air at 550°C for 10 h, is $Si_{63}Ge_{33}O_{192}$, as determined by atomic absorption and spot EDX analysis of individual crystallites.[8] In neutral or acidic media, other oxides, which contain most of the Ge, coprecipitate with the

[*] Dr. Z. Gabelica
Facultés Universitaires Notre-Dame de la Paix
Department of Chemistry
61, Rue de Bruxelles, B-5000 Namur (Belgium)

Dr. J. L. Guth
Laboratoire Matériaux Minéraux, E.N.S.C.Mu
F-68093 Mulhouse (France)