Ge$_8$O$_{16}$[(OH)$^-$(MeNH$_3$)$^+$(MeNH$_2$)]: one OH-templated germanium zeotype

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A new type of zeolite is found for the title microporous germanate whose peculiar connectivity between the 3- and 9-ring layers creates cages in which an extra-framework hydroxy group is confined.

Zeolites have found a number of applications in fields of commercial importance, notably as catalyst, adsorbents and ion exchangers.[1–4] Relating to the germanium zeotypes, the possibility of designing new open frameworks increases greatly due to the possible co-existence of different coordination polyhedra around Ge (tetrahedra, octahedra and trigonal bipyramid), which implies different charged frameworks without doping with trivalent cations. Nevertheless, novel microporous germanium frameworks had not been synthesized until recently.[5–11]

In terms of our interest in the structure–properties relationship for this kind of compound, we were concerned in the design and study of precise atomic architectures of zeotypes. In previous work the existence of Ge$_7$O$_{15}$$^{2-}$ (ICMM1)[12,13] and Ge$_9$O$_{19}$$^{2-}$ (ICMM2)[14] were reported. Here, we report the structure ICMM3, the first zeotype in which it is clear that one confined hydroxy group acts as a template.

ICMM3 was synthesized hydrothermally from a reaction mixture containing GeO$_2$, MeNH$_2$, H$_2$O and ethylene glycol in molar ratios 1 : 8 : 25 : 15. The mixture was introduced and sealed in a Teflon-lined stainless steel autoclave and heated at 170 °C for 4 days. After optimizing the reaction conditions, the yield was 100%. The purity of the resulting solid product was checked by X-ray powder diffraction.†

A suitable crystal of the compound with hexagonal platelike features was selected and mounted in a diffractometer equipped with a CCD detector. Crystals were pseudo-hexagonally twinned so that the space group appeared to have a pseudo-6$_3$ axis along *b*, however, the structure was solved and refined in the monoclinic space group *P*2$_1$ with *a* and *c* equal and β = 120°. Upon determining the crystal structure, the composition was found to be Ge$_8$O$_{16}$(OH)$^-$(MeNH$_3$)$^+$MeNH$_2$ in which the eight Ge atoms are at the center of more or less distorted tetrahedra [range of Ge–O bond lengths 1.72(2)–1.79(2) Å; O–Ge–O bond angles 95.5(7)–120.1(8)°, Ge–O–Ge 110.2(7)–143.5(7)°]. The tetrahedra are linked together in the *ac* plane giving rise to infinite GeO$_2$ layers which are constructed from a secondary structural building unit (SBU) denoted 4 = 1, joined by 3-tetrahedra rings into an infinite 9-tetrahedra ring containing sheet. This arrangement was also present in ICMM1 and in ICMM2. In the former zeotype, GeO$_6$ octahedra were involved in both 3- and 9-rings.

Every two GeO$_2$ adjacent sheets are joined through the three free oxygen atoms of the 3-ring tetrahedra creating thick blocks. These connections give rise to cages which are formed by six germanium atoms (three of each layer) and the three bringing oxygen atoms (Figs. 1 and 2). Inside these cages one atom of oxygen is found which corresponds to a confined OH$^-$ anion the hydrogen atom of which was located and isotropically refined [O–H 0.8(1) Å]. This oxygen interacts with the six germanium atoms of the cage at distances in the range 2.12(2)–2.44(2) Å. Depending on these distances the surrounding germanium polyhedra are distorted to a greater or lesser degree, distortion ranging from the nearly regular tetrahedron of

Ge(1) to what can be considered as trigonal bypiramids of Ge(4) and Ge(6) when including the fifth Ge–O interaction.

Cohesion between blocks is established, as also found in ICMM2, through the only oxygen atom [O(8)] not involved in connectivities within double layers. Also, as in ICMM2, the blocks are mutually shifted.

This 3D structure contains intersecting tunnels along the three directions: one set of tunnels runs in a zigzag fashion along the *b* direction as a consequence of the shifted pillaring of the 9R$_b$ 9-rings. Perpendicular to the *b* direction 8-ring 8R intersecting tunnels can be seen along the (101), (100) and (001) directions accordingly with the pseudo-hexagonal symmetry present in the crystals.

There are two crystallographically independent molecules of methylamine in the asymmetric unit, situated in the 8R channels
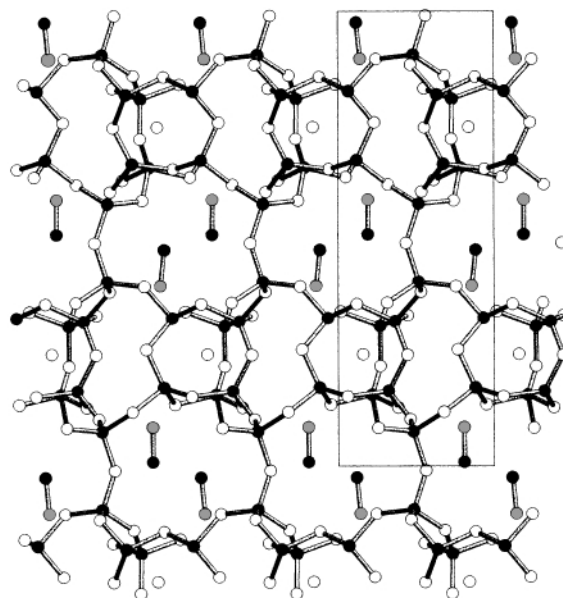
Fig. 1 View of the structure of ICMM3, showing the blocks and connectivity between them. Black, white and gray spheres are Ge, O and atoms of the amines, respectively.
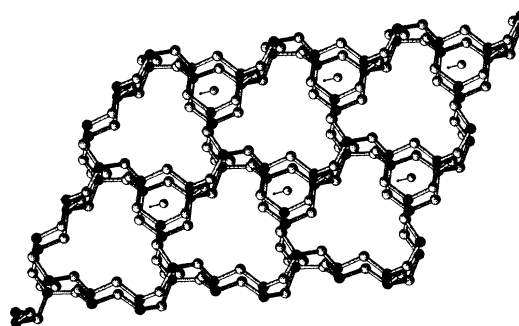
Fig. 2 View along the *b* direction of the double layer showing the confined OH group.

formed between blocks. They are bonded to different oxygen atoms of the framework through hydrogen bonds. Although hydrogen atoms involving amines could not be reliably located, the range of the N$\cdots$O distances [2.86(1)–3.08(1) Å], as well as their number, seem to indicate that many of these hydrogen bonds are bifurcated. Owing to the existence of one OH$^-$ anion, it is clear that to maintain electrical neutrality, a protonated amine is required. Protonation is established through the different C–N bond lengths [1.56(4) and 1.41(4) Å] as well as by spectroscopy. The IR spectrum shows a band at 3400 cm^{-1} due to the stretching vibrations of the OH groups while bands at 2792 and 2876 cm^{-1} arise from N–H vibrations, which are characteristic of a primary amine in its protonated form. Stretching vibrations of non-protonated amine sites occur at 3100 and 3164 cm^{-1}.

TGA–DTA in N$_2$ atmosphere (50 ml min^{-1}) shows one progressive weight loss between 375 and 550 °C accompanied by an endothermic effect corresponding to the loss of both methylamine molecules and the OH$^-$ group. Powder X-ray diffraction and IR spectra show that the structure is maintained upon heating to 375 °C during 4 h in air but collapses to give amorphous GeO$_2$ after prolonged heating.

In conclusion, a zeolite type microporous germanate has been synthesized. Its framework exhibits a peculiar connectivity between the 3- and 9-ring layers. Every two of these layers are joined through the three free oxygen atoms of the 3-ring tetrahedra. This joining creates cages in which an extra-framework hydroxy group is trapped. The negative charge of this OH$^-$ group is compensated by one intratunnel protonated methylamine molecule.

Notes and references

1 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
2 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
3 J. M. Thomas, *Angew. Chem., Int. Ed.*, 1999, **38**, 3588.
4 T. E. Gier, X. Bu, P. Feng and G. D. Stucky, *Nature*, 1998, **395**, 154.
5 H. Li, M. Eddaoudi, D. A. Richardson and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8567.
6 H. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 10 569.
7 X. Bu, P. Feng and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 11204.
8 X. Bu, P. Feng, T. E. Gier, D. Zhao and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 13 389.
9 H. Li, M. Eddaoudi and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 1999, **38**, 653.
10 M. O'Keeffe and O. M. Yaghi, *Chem. Eur. J.*, 1999, **5**, 2796.
11 X. Bu, P. Feng and G. D. Stucky, *Science*, 1997, **278**, 2080.
12 C. Cascales, E. Gutiérrez-Puebla, M. A. Monge and C. Ruiz-Valero, *Angew. Chem.*, 1998, **110**, 135; C. Cascales, E. Gutiérrez-Puebla, M. A. Monge and C. Ruiz-Valero, *Angew. Chem., Int. Ed.*, 1998, **37**, 129.
13 C. Cascales, E. Gutiérrez-Puebla, M. A. Monge and C. Ruiz-Valero, *Int. J. Inorg. Mater.*, 1999, **1**, 181.
14 C. Cascales, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge and C. Ruiz-Valero, *Angew. Chem.*, 1999, **111**, 2592; C. Cascales, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge and C. Ruiz-Valero, *Angew. Chem., Int. Ed.*, 1999, **38**, 2436.
15 SHELXTL, Siemens Energy & Automation Inc., Analytical Instrumentation, 1996.