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A germanium zeotype with a three-dimensional net of interconnected 14-, 12- and 12-ring channels. $Ge_{13}O_{26}(OH)_4[C_6N_2H_{16}]_2(H_2O)_{1.5}$

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$Ge_{13}O_{26}(OH)_4[C_6N_2H_{16}]_2(H_2O)_{1.5}$ is a novel germanium zeotype built up from a new type of SBU; the SBU-13 is formed from polyhedra distributed in three shells. Its open 3D framework has a three-dimensional system of intersecting channels, where the 14-ring channels are lined with OH^- anions.

In the early 1990s, three interesting germanates[1] were reported, but it was not until the end of the decade that interest in the microporous germanium zeotypes appeared with great force,[2,3] so that in the last six years about thirty papers on the purely Ge–O system have been reported.[4,5] In these zeotypes the secondary building unit (SBU) can be formed by Ge atoms in tetrahedral, trigonal bipyramidal and octahedral coordination, these polyhedra being connected by sharing vertices, edges or faces. Anions (oxide ions or hydroxyl groups) are also frequently in 1-, 2-, or 3-coordination. This variability in coordinative modes allows for the generation of many different SBUs, different kinds of connection among them, and thus, a plethora of structural possibilities. Here we report ICMM7, a new zeotype of germanium wrought by an asymmetric amine, with a structure derived from motifs each composed of 13 polyhedra (SBU-13), and 14-ring (14R) channels.

Our interest being in the influence of the hydroxyl group on zeotype formation, we have reported the existence of OH^- anions encapsulated inside the framework cages,[6,7] as well as others in which the hydroxyl group is bonded occupying the fifth coordination position of a GeO_5 pentacoordinated species to give a laminar structure.[8] ICMM7 is a germanium zeotype, in which the OH^- anions are lining the 14R channels.

The title compound was synthesized hydrothermally in a stainless steel autoclave from reaction mixtures containing GeO_2, 4-aminomethylpiperidine, H_2O and 1-butanol (molar ratio of reactants 1 : 2 : 56 : 28) at 180 °C over 7 days. pH values of the initial and final mixtures were about 12 and 9.5–10, respectively. After optimising the reaction conditions, ICMM7 was obtained as the only product of the reaction. The purity of the resulting solid was checked by X-ray powder diffraction.

Upon determining the crystal structure†, the composition was found to be $Ge_{13}O_{26}(OH)_4[C_6N_2H_{16}]_2(H_2O)_{1.5}$ (ICMM7).

The asymmetric unit of ICMM7 is formed by 13 Ge atoms, 30 oxygen atoms, 2 $[C_6N_2H_{16}]_2^{2+}$ cations, and 1.5 water molecules. Nine germanium atoms are in tetrahedral coordination environments, and the remaining four are situated in the center of octahedra (Fig. 1). These latter four form Ge_4O_{16} tetrameric units, in which each octahedron shares three edges enclosing a tetrahedral hole at the center. The tetramers, with cubic ($43m$, T_d) symmetry, are sharing their 12 free oxygen atoms with 6 tetrahedral germanium atoms to give $[Ge_{10}O_{28}]$ SBU-10 motifs (Fig. 2). This SBU-10 appears also in the $Ge_7O_{16}^{4+}$ framework with the pharmacosiderite structure type (Fig. 2). In that structure these units keep the $43m$ symmetry, and interconnect three-dimensionally in a cubic structure. In ICMM7, a tilting of the tetrahedra breaks the cubic symmetry, and allows, at the same time, a connection among units that gives rise to puckered double layers perpendicular to the [001] direction (Fig. 3).

The side of each SBU-10 that points outside the double layer is surrounded by three more tetrahedral Ge atoms; two of them, $GeO_2(OH)_2$, are not involved in more connectivity, and the remaining GeO_4 is the only one that connects the double layers to each other. In this way, the actual SBUs existing in the current compound can be depicted as a SBU-13, or better as a SBU-(10 + 3), whose polyhedra are distributed in three shells (4Oh + 6Th + 3Th) (Fig. 2). An alternative description[9] is to consider the SBU-13 as formed by two SBUs, one SBU-8 also very close to that of the pharmacosiderite, but with 4 tetrahedra (those that are in the

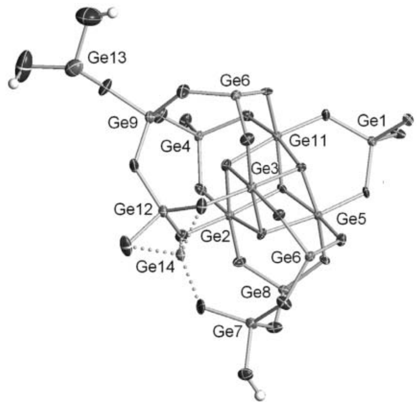

Fig. 1 Ortep plot of the asymmetric unit.

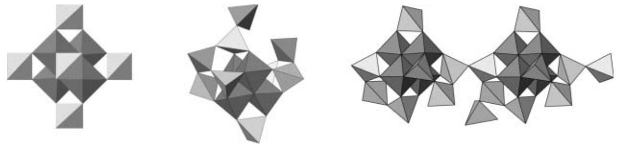

Fig. 2 Polyhedral representation of: (left side) SBU-10 in pharmacosiderite, (center) the new SBU-13, and (right side) composition of two SBU-8 motifs and one bridging pentagermanate SBU-5.

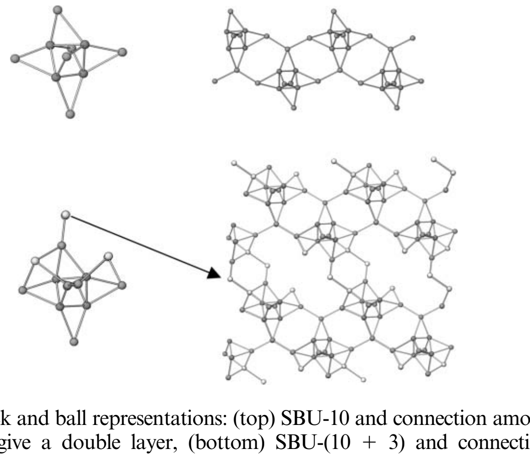

Fig. 3 Stick and ball representations: (top) SBU-10 and connection among them to give a double layer, (bottom) SBU-(10 + 3) and connection of layers.

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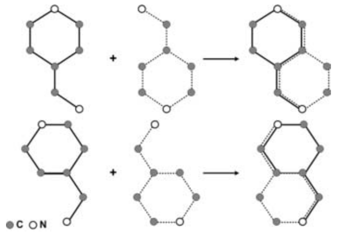

Scheme 1

equatorial plane), instead of the six ones, and the other formed by a cluster of five tetrahedra, a pentagermanate (Fig. 2).

Distances Ge–Ge in this SBU are within the range 2.94–3.14 Å. The result is an open 3D framework with a three-dimensional system of intersecting channels: 14R (14.5 × 8.5 Å) and 6R run along the *a* direction, 12R (11.6 × 5.3 Å) and 8R (8.3 × 8.7 Å) along the *b* direction. Additionally, and as a result of this intersection, other channels of dimensions 11.6 × 10.5 Å can be seen looking at the structure along the [$1\bar{1}0$] direction. (lengths are given between atom centers). Parallel to the *c* direction run 6R and 12R channels too. 14R channels are not very frequent, in fact, only five zeolites (CFI, DON, OSO, SFH, and SFN),[10] and one zirconogermanate[11] with this kind of channel have been reported, and none of them has a 14R × 12R × 12R three dimensional system of tunnels. ICMM7 is thus, to the best of our knowledge, the first zeotype with such characteristics.

Some positional disorder has been found around Ge12; refinements of this atom at the positions named as Ge12 and Ge14 give population factors of 0.91 and 0.09, respectively. As this atom is not involved in connectivity in the frame, this disorder does not imply variation of the structure other than a small difference in the tilting of this tetrahedron in 9% of their crystallographic positions.

Protonated molecules of amine run along the 8R and 14R intercrossing channels. Those that run along the [010] direction inside the 8R tunnels are positionally disordered. The model established to solve this disorder is shown in Scheme 1. The cationic molecules situated in the 14R along the [100] direction are perfectly ordered (Fig. 4).

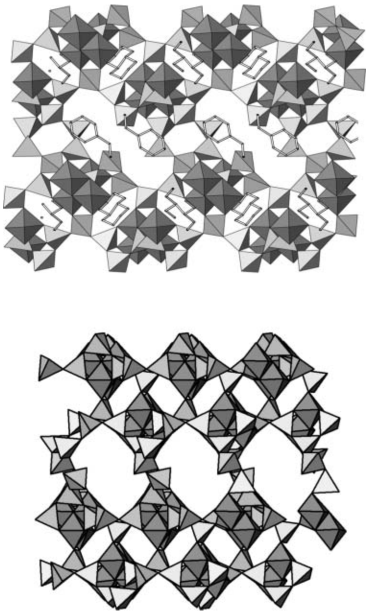

Fig. 4 Polyhedral representations of ICMM7, showing: (top) the ordered amine molecules in the 14R channels and those disordered in the 8R, (bottom) a view of the channels along the [$1\bar{1}0$] direction.

Walls of 14R channels are OH^- lined, since all the hydroxyl groups of the $GeO_2(OH)_2$ tetrahedra point toward the 14R inter-channel space. This fact makes these tunnels more hydrophilic than the others, and thus, it is inside them where a net of hydrogen bonds among the framework, the housed water molecules, and the nitrogen atoms of the amine molecules, prevents disorder of their guest molecules.

TGA-DTA analyses of ICMM7 showed that it is stable up to 250 °C. A progressive weight loss of 20% is observed, that corresponds to the loss of two H_2O, two $[C_6N_2H_{16}]_2^{2+}$ and four OH groups per formula unit. After that the structure collapses into GeO_2, as usually happens in this type of zeotype due to the decomposition of the entrapped molecules. The presence of both OH^- anions, (stretching band centered at 3500 cm^{-1}) and protonated amine (bands centered at 2500 cm^{-1}, and 1530 cm^{-1}) are observed in the IR spectrum of ICMM7.

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Notes and references

† Crystal data for $Ge_{13}O_{26}(OH)_4[C_6N_2H_{16}]_2(H_2O)_{1.5}$ (ICMM7) $M = 1687.1$, triclinic space group: $P\bar{1}$; $a = 10.473(4)$, $b = 12.601(5)$, $c = 15.550(6)$ Å; $\alpha = 86.071(1)°$, $\beta = 79.162(1)°$, $\gamma = 83.780(1)°$; $V = 2001.6(1)$, Å^3; $Z = 2$; $D_c = 2.799$ Mg m^{-3}; μ(Mo–Kα) = 9.713 mm^{-1}; dimensions 0.1 × 0.1 × 0.04 mm. Number of independent reflections = 9719; $R_1 = 0.048$ for $I > 2\sigma(I)$ reflections. The population factors of Ge12 and Ge14 were refined constrained to add up to unity. One of the aminomethylpiperidine molecules is involved in positional disorder, consequently the population factors were introduced on the basis of the thermal parameter values following the model of disorder given in the paper. Hydrogen atoms of the OH groups were located in difference Fourier maps, except for the one involved in tetrahedron disorder. The hydrogen atoms of the water molecules could not be accurately located. Software for the SMART System V5.04 and SHELXTL V 5.1 were used, Bruker-Siemens Analytical X-ray Instrument Inc., Madison, WI, 1998. CCDC 247518. See http://www.rsc.org/suppdata/cc/b4/b409668a/ for crystallographic data in .cif or other electronic format.

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