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GeO_2 Natrolite-Type Infinite Four and Eight R-Containing Layers in a 2D Pure-Ge Framework: $Ge_3O_5(OH)_4[C_2N_2H_{10}]$

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A new two-dimensional framework germanate, $Ge_3O_5(OH)_4[C_2N_2H_{10}]$ (denoted ICMM-8), with a 3:9 Ge:O ratio has been synthesized, using a mixture of pyridine, water, and ethanol as the solvent and 1,4-diazabicyclo[2.2.2]octane and ethylenediamine as the structure-directing agents, under solvothermal conditions. The structure was determined by single-crystal X-ray diffraction. In this new compound, the GeO_2 natrolite-type infinite four and eight R-containing layers appears for the first time in a pure GeO_2 framework. The total 2D structure is built up from SBU-6, four tetrahedra, and two octahedra. The hydroxyl groups occupy four positions of each octahedral germanium atom. The compound is characterized by IR spectra and TGA-DTA. Crystal data: $Ge_3O_5(OH)_4[C_2N_2H_{10}]$, monoclinic space group $P2_1/c$; $a = 11.3570(9)$ Å, $b = 8.8819(7)$ Å, $c = 9.9200(8)$ Å, $\beta = 90.710(1)$, $V = 1000.6(1)$ Å^3, $Z = 4$, $R_1 = 0.044$ ($I > 2(I)$), and $wR_2 = 0.1051$ (all data).

Introduction

Zeolites, the most well-known family of porous materials, belong to an important family of solids with immense applications in catalysis, ion exchange, and gas separation. In open-framework germanates, germanium analogues of zeolite, in contrast to normally tetrahedrally coordinated silicon, germanium can form a variable and expanded coordination environment because of the large Ge:O radius ratio. Anions (oxygen atoms or hydroxyl groups) are also frequently presented in 1-, 2-, or 3-coordination environments, and thus a great number of novel structures can potentially be obtained. During the past decade, a number of new porous germanates have been obtained whose structures consist of pure tetrahedral or mixed polyhedra.[1−4]

Our interest is in the influence of the hydroxyl group in the zeotype formation. We have reported the existence of OH anions encapsulated inside the framework cages,[5,6] as well as others in which the hydroxyl group is bonded and occupies the fifth coordination position of $GeO_4(OH)$ pentacoordinated species, giving a laminar structure,[7] or forms OH-lined 14 R-channels via $GeO_2(OH)_2$ tetrahedra.[8] Although several zeotypes formed by ethylenediamine have been reported,[2,9,10] none of them has a lamellar structure. Here, we report ICMM-8, an ethylenediamine-templated 2D germanate in which the hydroxyl groups occupy four positions of an octahedral germanium atom.

Experimental Section

General Information. All reagents were commercially available (GeO_2, 99%; 1,4-diazabicyclo[2.2.2]octane (DABCO), 98%; ethylenediamine (En), 99%; pyridine (Py), 99%; ethanol, 99.95%; all

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from Aldrich) and used as received. The IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Perkin-Elmer spectrometer. Thermogravimetric and differential thermal analyses (TGA-DTA) were performed using a SEIKO TG/DTA 320 apparatus in the temperature range 25−800 °C in O_2 (flow of 50 mL min^{-1}) with a heating rate of 5 °C/min.

Synthesis and Characterization. ICMM-8 was synthesized in the GeO_2−En−DABCO−Py−water−ethanol reaction system with an approximate optimized GeO_2:En:DABCO:Py:water:ethanol molar composition range of 1.0:1.0:3.0:4.0:90.0:90.0. Typically, 1.0 g of GeO_2 was dispersed into 15 mL of water with stirring followed by the addition of 0.48 g of En and 3.0 g of DABCO. Pyridine (3 mL) and ethanol (50 mL, 99.5%) were added to the above reaction mixture while it was being stirred. The reaction mixture was stirred until it was homogeneous; it was then sealed in a Teflon-lined stainless autoclave and heated under autogenous pressure at 170 °C for 5 days. The pH value of the initial mixture was about 8.5. The resulting product, containing colorless crystals, was separated using filtration, washed with deionized water and acetone, and dried at room temperature. The yield of the product was about 75% on the basis of the source of GeO_2.

Structure Determination. Data for a colorless single crystal of ICMM-8 were collected in a Siemens SMART-CCD diffractometer over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in ω. Data were collected using a ω scan over the range $2° < \theta < 28°$. The total number of reflections measured was 8418, of which 2426 were independent. The structure was solved by direct methods. Refinement was carried out by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in a Fourier map and isotropically refined. The final residuals were $R_F = 0.04$ for $I > 2\sigma(I)$ and 0.05 for all data. Data processing was accomplished with the SAINT processing program. Calculations were carried out with SMART software for data collection and data reduction and the SHELXTL crystallographic software package.[11] Data collection and refinement details, coordinates, and selected bond lengths and distances are listed in Tables 1, 2, and 3, respectively.

Results and Discussion

ICMM-8 is one more result of our investigations on GeO_2−amine−H_2O−alcohol systems. From previous work,[10] we learned that in the system GeO_2−DABCO−H_2O−BuOH, a chiral germanium zeotype (ICMM-7) was formed. This latter germanate housed double-charged ethylenediamine molecules (released through DABCO molecule decomposition in a hydroalcoholic medium). The same framework is also obtained[10] when directly using ethylenediamine instead of DABCO, with the other conditions unchanged.

In the system GeO_2−DABCO−En−H_2O−EtOH, under the synthesis conditions indicated above, the new ICMM-8 appears. It is worth mentioning in this case that in the absence of En in the starting mixture (i.e., in DABCO−GeO_2−EtOH−H_2O reaction mixture), the only product obtained is ICMM-5.[6] On the other hand, if DABCO is absent in the initial reaction mixture or is replaced by another organic amine, pure GeO_2 or known germanium zeotypes are formed. Table 4 gives the screening results in the GeO_2−amine mixture−H_2O−EtOH system.

Table 1. Crystal Data and Structure Refinement for $Ge_3O_5(OH)_4(C_2N_2H_{10})$

identification code	ICMM-8
empirical formula	C2 H14 Ge3 N2 O9
fw	427.92
T (K)	296(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	$P2(1)/c$
a (Å)	11.3570(9)
b (Å)	8.8819(7)
c (Å)	9.9200(8)
α (deg)	90
β (deg)	90.710(1)
γ (deg)	90
Z	4
V (Å^3)	1000.5(1)
d_{calcd} (Mg/m^3)	2.841
abs coeff (mm^{-1})	8.996
F(000)	832
cryst size (mm^3)	0.15 × 0.15 × 0.10
θ range for data collection (deg)	1.79−28.32
index ranges	$-15 < h < 15$, $-11 < k < 11$, $-13 < l < 12$
no. of reflns collected	8418
no. of independent reflns	2426 [R(int) = 0.1281]
completeness to $\theta = 28.32°$ (%)	97.6
refinement method	full-matrix least-squares on F^2
data/restraints/params	2431/8/161
GOF on F^2	1.101
final R indices [$I > 2\sigma(I)$]	R1 0.0442, wR2 0.1070
R indices (all data)	R1 0.0546, wR2 = 0.1117
largest diff. peak and hole (e Å^{-3})	1.020 and −1.093

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2, ×10^3)

	x	y	z	U(eq)[a]
Ge(1)	10682(1)	1982(1)	9379(1)	12(1)
Ge(2)	9741(1)	4064(1)	7144(1)	12(1)
Ge(3)	7096(1)	5290(1)	6863(1)	15(1)
O(1)	9724(4)	782(5)	8462(5)	17(1)
O(2)	12052(4)	1181(6)	9481(5)	20(1)
O(3)	10035(5)	2320(5)	10936(5)	17(1)
O(4)	10609(4)	3749(5)	8588(5)	17(1)
O(5)	8259(4)	4024(6)	7508(5)	22(1)
O(6)	6144(4)	4396(6)	8086(5)	16(1)
O(7)	7489(5)	6689(5)	8099(5)	19(1)
O(8)	5852(4)	6412(5)	6355(5)	17(1)
O(9)	6588(4)	3877(5)	5670(5)	15(1)
C(1)	6731(8)	107(9)	6112(8)	25(2)
N(1)	7617(6)	1076(8)	5455(7)	27(1)
N(2)	6041(6)	−819(8)	8290(7)	25(1)
C(2)	6752(8)	368(9)	7622(8)	27(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor.

All in all, and even though it is not included in the final product, DABCO plays an important structure-directing role in the formation of ICMM-8. This phenomenon is commonly observed in the synthesis of zeolite and zeolite-like materials, such as $AlPO_4$-15 and AlPO-CJ4.[11,12] On the other hand, a gradual increase in En concentration has a definitive influence on the final formation of ICMM-8.

Attempts to intercalate other amines (using an amine other than En, e.g., dimethylamine, methylethylamine, 1,2-diaminopropane, *N,N′*-diisopropylethylenediamine, or 1,2-diaminocyclohexane) into the ICMM-8 framework resulted in the formation of only GeO_2.

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Table 3. Bond Lengths (Å) and Angles (deg) for $Ge_3O_5(OH)_4(C_2N_2H_{10})$[a]

Ge(1)−O(4)	1.756(4)	Ge(2)−O(1)#2	1.752(5)
Ge(1)−O(2)	1.713(5)	Ge(3)−O(8)	1.795(4)
Ge(1)−O(3)	1.744(5)	Ge(3)−O(7)	1.798(5)
Ge(1)−O(1)	1.767(5)	Ge(3)−O(9)	1.814(4)
Ge(2)−O(4)	1.752(5)	Ge(3)−O(6)	1.818(5)
Ge(2)−O(5)	1.726(5)	Ge(3)−O(2)#2	1.837(5)
Ge(2)−O(3)#1	1.751(5)	Ge(3)−O(5)	1.844(5)
O(2)−Ge(1)−O(3)	114.3(2)	O(7)−Ge(3)−O(9)	175.7(2)
O(2)−Ge(1)−O(4)	115.8(3)	O(8)−Ge(3)−O(6)	87.6(2)
O(3)−Ge(1)−O(4)	102.9(2)	O(7)−Ge(3)−O(6)	89.5(2)
O(2)−Ge(1)−O(1)	109.4(2)	O(9)−Ge(3)−O(6)	86.9(2)
O(3)−Ge(1)−O(1)	107.2(2)	O(8)−Ge(3)−O(2)#2	88.7(2)
O(4)−Ge(1)−O(1)	106.5(2)	O(7)−Ge(3)−O(2)#2	93.9(2)
O(5)−Ge(2)−O(3)#1	108.9(3)	O(9)−Ge(3)−O(2)#2	89.5(2)
O(5)−Ge(2)−O(1)#2	115.6(2)	O(6)−Ge(3)−O(2)#2	174.9(2)
O(3)#1−Ge(2)−O(1)#2	107.9(2)	O(8)−Ge(3)−O(5)	173.6(2)
O(5)−Ge(2)−O(4)	111.5(2)	O(7)−Ge(3)−O(5)	90.8(2)
O(3)#1−Ge(2)−O(4)	109.7(2)	O(9)−Ge(3)−O(5)	91.4(2)
O(1)#2−Ge(2)−O(4)	103.1(2)	O(6)−Ge(3)−O(5)	86.1(2)
O(8)−Ge(3)−O(7)	89.8(2)	O(2)#2−Ge(3)−O(5)	97.6(2)
O(8)−Ge(3)−O(9)	87.6(2)		

[a] The following symmetry transformations were used to generate equivalent atoms: #1 = $x, -y + {}^1/_2, z - {}^1/_2$; #2 = $-x + 2, y + {}^1/_2, -z + {}^3/_2$; #3 = $-x + 2, y - {}^1/_2, -z + {}^3/_2$; #4 = $x, -y + {}^1/_2, z + {}^1/_2$.

Table 4. Results from Screening in the GeO_2−En−Cyclic Amine−Py−H_2O−EtOH System[a]

cyclic amine	pH	final products
DABCO[b]	8.0	ASU-9[17] + ICMM-8 (traces)
DABCO	8.5	ICMM-8 + ICMM-6 (traces)
piperazine	8.0	ASU-14[18]
homopiperazine	8.0	ICMM-6 + GeO_2 (traces)
1-methylpiperazine	8.5	ICMM-6 + GeO_2
hexamethylenetetramine	8.5	GeO_2
1-(2-amino-ethyl)pyrrolidine	8.5	GeO_2
piperidine	8.5	GeO_2

[a] The molar composition range was always 1.0:1.0:3.0:4.0:90.0:90.0 GeO_2:En:Cyclic Amine:Py:H_2O:EtOH. [b] The concentration of En was 0.25 mol.

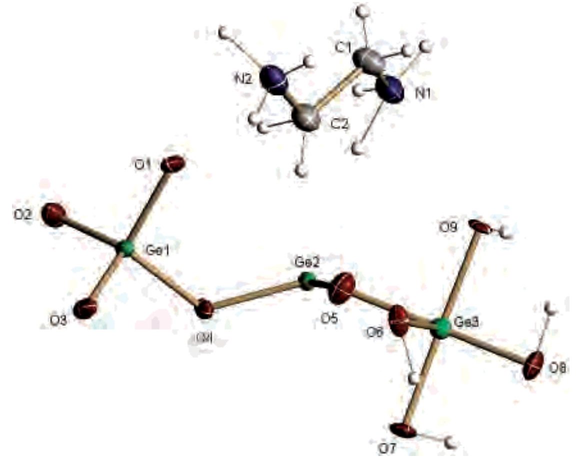

Figure 1. Ortep plot of the ICMM-8 asymmetric unit.

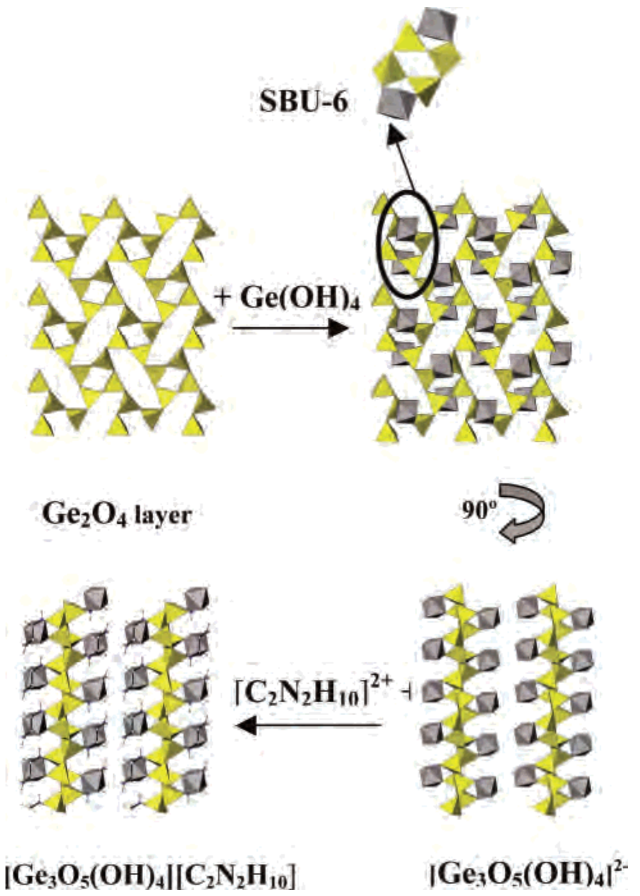

Figure 2. Polyhedral representations of ICMM-8 showing the GeO_2 infinite four and eight R-containing layers, the complete $[Ge_3O_5(OH)_4]^{2-}$ sheets, and the protonated ethylenediamine molecules hydrogen bonded to the framework oxygen atoms.

Table 5. Hydrogen Bonds and Main Interaction Geometry

X−H$\cdots$O	X−H (Å)	X$\cdots$O (Å)	H$\cdots$O (Å)	X−H$\cdots$O (deg)
N1−H101$\cdots$O5[a]	0.97	3.03	2.17	145.7
N1−H101$\cdots$O6[a]		2.90	2.14	133.7
N1−H102$\cdots$O4	0.64	3.03	2.57	138.3
N1−H103$\cdots$O3[a]	1.16	3.12	2.27	127.7
N1−H103$\cdots$O5[a]		3.03	2.32	151.1
N2−H201$\cdots$O6	0.87	2.82	1.99	158.7
N2−H202$\cdots$O9	0.87	2.90	2.29	135.1
N2−H203$\cdots$O7	1.16	2.98	1.66	160.4
O9−H9$\cdots$O2	0.99	2.57	1.94	119.3

[a] Bifurcated hydrogen bonds.

Upon determining the crystal structure, we found the composition to be $Ge_3O_5(OH)_4[C_2N_2H_{10}]$ (ICMM-8). Its asymmetric unit thus comprises three Ge atoms, five oxygen atoms, four hydroxyl groups, and one $[C_2N_2H_{10}]^{2+}$ cation (Figure 1). Two germanium atoms per formula are in a tetrahedral coordination, forming centrosymmetric sharing vertex Ge_4O_{12} cyclogermanates. The third Ge atom is octahedral and bonded to four hydroxyl groups and two tetrahedra, by sharing the only remaining oxygen in each tetrahedron. The result is the formation of secondary building units with six polyhedra SBU-6 and −1 internal symmetry (Figure 2). One protonated ethylenediamine cation surrounds each octahedron, strongly bonded through hydrogen bonds to the inorganic framework. Table 5 shows the hydrogen bond geometry, as well as the two longer N−H distances (1.16 Å) for the amine protons.

The tetrameric Ge_4O_{12} units form, also by sharing vertexes, GeO_2 infinite four and eight R-containing layers, similar to that in the natrolite type.[14] The $GeO_2(OH)_4$ octahedra

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(14) Database of zeolite structures http://www.iza-structure.org/databases. Structure Commission of the International Zeolite Association.

decorate both sides of the layers accordingly with the centrosymmetric symmetry, without changing the lamellar character of ICMM-8.

It is worth mentioning that this kind of four and eight R-containing layer arrangement, which is present in zeolites, ALPOs, and some metallogermanates,[15] has not been observed, to the best of our knowledge, in pure germanium zeotypes, in which the three−nine ring association seems to be more frequent.[1] In these latter materials, in which Ge_4O_{12} cyclogermanates exist, they form cubane 4−4 units[6,16] or are linked among them through other germanium polyhedra.[7] In the previously reported lamellar ICMM-4, the tetramers are kept together through trigonal bipyramids to give 4 and 10 rings that are also in a 2D structure.

TGA-DTA (TGA = thermogravimetric analysis, DTA = differential thermal analysis) in O_2 flow shows that the compound is stable up to 340 °C. A progressive weight loss of ∼26.9% is observed between 340 and 400 °C, accompanied by two endothermic peaks corresponding to the loss of the ethylenediamine molecule and three water molecules successively (calcd: 26.65%). After that, the structure collapses into GeO_2, as usually happens in this type of zeotypes because of the loss of the entrapped cationic molecules. X-ray powder diffraction indicates that the final product is crystalline germanium dioxide.

Taking into account the indicated thermal stability and given that the germanium octahedra contains hydroxyl groups that could be induced to combine, forming an extended structure, we have tested this possibility (mild heating at 200° for 1, 2, and 3 h). X-ray powder diffraction showed no change in the structure. The result is not surprising given the ionic character of ICMM-8 that forces structural destruction with the loss of the amine cations and prevents any kind of structural reorganization below the decomposition temperature.

The presence of both OH^- anions (stretching band centered at 3500 cm^{-1}) and protonated amine (bands centered at 2500 and 1530 cm^{-1}) is observed in the IR spectrum of ICMM-8.

In summary, a new two-dimensional germanium framework, $Ge_3O_5(OH)_4[C_2N_2H_{10}]$ (ICMM-8), with a 3:9 Ge:O ratio, has been synthesized. Its structural original features are as follows: the arrangement of four and eight tetrahedral ring-containing sheets not previously observed in pure germanium zeotypes and the alternation of $[Ge_3O_5(OH)_4]^{2-}$ infinite inorganic sheets and protonated ethylenediamine cations.

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Supporting Information Available: Crystallographic data (CIF) for ICMM-8. This material is available free of charge via the Internet at http://pubs.acs.org.

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