Synthesis and Structure of a New Microporous Anionic Derivative of GeO_2: $[Ge_{18}O_{38}(OH_4)]^{8-}[(C_2N_2H_{10})^{2+}]_4 \cdot 2H_2O$

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The preparation and characterization of a novel, crystalline, microporous germanium oxide in which Ge exhibits 4-, 5-, and 6-fold coordination are described; its framework structure contains two types of oval 10-membered-ring and one type of 8-membered-ring channels which intersect one another, the largest diameter of the oval framework windows being 5.2 Å.

Introduction

Catalysts, sorbents, and sensors derived from naturally occurring three-dimensionally extended and layered aluminosilicates have wide utility,[1,2] and there is growing interest in the possibility of synthesizing new microporous materials based on elements other than silicon and/or aluminium.[3] Recent attention has focused on III–V microporous oxides such as aluminum phosphates ($AlPO_4$s),[4] gallium phosphates ($GaPO_4$s),[5] and zinc phosphates[3] in which the non-oxygen atoms are usually, but not invariably,[6] tetrahedrally coordinated. However, there are surprisingly few reports of microporous germanates, the only fully characterized systems being $(M_{3+x}H_{1-x})^- Ge_7O_{16} \cdot nH_2O$ (M = Li, Na, K, Rb, Cs, and NH_4) and $[Ge_6O_{12}(OH)]^-[N(CH_3)_4]^+$. The former[7,8] has intersecting channels with eight-ring—i.e., eight oxygen as well as eight germanium atoms—apertures that run in three intersecting directions and possess tetrahedrally coordinated Ge atoms. In the latter,[9] the Ge atoms exist in either tetrahedra or trigonal bipyramids formed by oxygen atoms and there are intersecting four-, six-, and eight-membered rings. Some other organic templates including ethylenediamine and propylenediamine were also successfully used[10] for the preparation of framework germanates, but previously the size of the crystalline products has been too small for single-crystal structure analysis. By changing the crystallization conditions, we have successfully prepared large single crystals of the ethylenediamine-occluding germanate. Here we report the synthesis and structural characterization of this novel microporous derivative of germanium oxide possessing medium-sized pores.

Table I. Crystallographic Data for $[Ge_{18}O_{38}(OH)_4]^{8-}[(C_2N_2H_{10})^{2+}]_4 \bullet 2H_2O$

chem formula	$[Ge_{18}O_{38}(OH)_4]^{8-}[(C_2N_2H_{10})^{2+}]_4 \cdot 2H_2O$
formula wt	2267.11
crystal system	orthorhombic
space group	$P2_12_12_1$
a, Å	12.135 (3)
b, Å	14.230 (1)
c, Å	27.857 (11)
V, Å^3	4810.4
Z	4
crystal size, mm	0.28 × 0.11 × 0.14
D_{calc}, g cm^{-3}	3.131
radiation	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	110.43
θ_{min}(all data), deg	22.35
reflections measd	16592
unique reflections	6422
reflections obsd	4031
criterion for observation	$F > 3\sigma(F)$
transmission coefficients	0.941–1.286
no. of parameters	403
R	0.035
R_w	0.041

Experimental Section

The title compound was synthesized under hydrothermal conditions in the presence of ethylenediamine (en). Quartz type GeO_2 (2 g) was added to a solution obtained by mixing 6 mL of en and 13 mL of water. The mixture was stirred until the GeO_2 was dissolved completely. The pH value of the final solution, which had an empirical composition of GeO_2:4.70en:37.5H_2O, was higher than 12. This solution was then sealed in a Teflon-lined autoclave and heated at 180–200 °C for 6 days under autogeneous pressure. The product which appeared to be uniform gave needlelike crystals with typical dimensions of 0.2 × 0.3 × 1.0 mm, was filtered, washed with distilled water, and dried at ambient temperature. With increasing en/GeO_2 ratios in the reactant mixtures the crystallization time decreased but the product crystals were much smaller, irregular in shape, and much less transparent. Longer crystallization times and/or higher crystallization temperatures can result in the formation of dense GeO_2 phases from the reaction mixtures. From TGA-DTA analysis, the as-synthesized compound exhibits a distinct endotherm at about 400 °C. This is believed to correspond to the decomposition of the occluded template. After calcination at 350 °C for 40 min,

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Table II. Fractional Atomic Coordinates (10^4) and Equivalent Isotropic Thermal Parameters (10^3) with Esds in Parentheses for the Non-Hydrogen Atoms

atom	*x/a*	*y/b*	*z/c*	*U*(iso)	atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Ge(1)	2512.9 (9)	9898.7 (7)	7971.3 (5)	70	O(22)	331 (8)	10813 (5)	6842 (3)	172 (18)
Ge(2)	7477 (1)	10000.6 (7)	10477.7 (5)	90	O(23)	1429 (8)	12185 (5)	7572 (4)	257 (22)
Ge(3)	4638 (1)	8455.7 (7)	7378.1 (5)	110	O(24)	806 (8)	9383 (5)	6261 (3)	163 (19)
Ge(4)	3869 (1)	10107.5 (7)	6882.2 (5)	92	O(25)	623 (7)	8697 (5)	7119 (3)	121 (17)
Ge(5)	432 (1)	11361.6 (7)	7414.3 (5)	101	O(26)	5774 (9)	9426 (5)	8770 (4)	223 (20)
Ge(6)	1173 (1)	9760.3 (7)	6867.9 (6)	97	O(27)	7475 (7)	10114 (4)	9168 (4)	159 (18)
Ge(7)	6139 (1)	9849.0 (7)	9365.5 (5)	82	O(28)	5723 (8)	8738 (5)	9596 (3)	140 (17)
Ge(8)	−1149 (1)	10149.4 (7)	9382.2 (5)	78	O(29)	5183 (7)	10800 (4)	9347 (3)	86 (16)
Ge(9)	5397 (1)	11482.9 (7)	9881.6 (5)	103	O(30)	−680 (9)	10514 (5)	8789 (3)	208 (19)
Ge(10)	−486 (1)	8494.2 (7)	9918.4 (5)	113	O(31)	−665 (8)	11228 (5)	9615 (3)	171 (18)
Ge(11)	4934 (1)	9659.7 (6)	8290.9 (6)	89	O(32)	−301 (7)	9128 (5)	9352 (3)	140 (17)
Ge(12)	4234 (1)	11422.8 (7)	7741.8 (5)	87	O(33)	358 (8)	8802 (5)	5407 (3)	141 (18)
Ge(13)	734 (1)	8414.4 (7)	7722.9 (5)	87	O(34)	4452 (7)	12338 (5)	9645 (3)	143 (17)
Ge(14)	86 (1)	10132.9 (7)	8314.9 (6)	91	O(35)	6491 (8)	12237 (5)	9982 (4)	215 (21)
Ge(15)	5689 (1)	8566.4 (7)	10224.2 (5)	105	O(36)	4677 (7)	11171 (5)	5414 (3)	124 (17)
Ge(16)	−60 (1)	9684.6 (7)	5798.4 (6)	102	O(37)	421 (7)	7618 (4)	9660 (3)	125 (17)
Ge(17)	−733 (1)	11475.3 (7)	10237.3 (5)	97	O(38)	−1549 (8)	7712 (5)	10087 (3)	208 (21)
Ge(18)	5094 (1)	10285.1 (7)	5810.8 (6)	100	O(39)	5286 (7)	10765 (5)	8055 (3)	157 (17)
O(1)	1455 (7)	10265 (4)	7510 (3)	125 (18)	O(40)	−238 (7)	8990 (4)	8105 (3)	125 (17)
O(2)	3625 (7)	9618 (4)	7526 (3)	116 (17)	O(41)	311 (8)	10787 (5)	5536 (3)	176 (18)
O(3)	3545 (8)	9583 (5)	8466 (3)	160 (18)	O(42)	4722 (8)	9186 (5)	5546 (3)	158 (18)
O(4)	2979 (6)	11172 (4)	8011 (3)	37 (15)	N(1)	2665 (11)	8458 (7)	5848 (4)	346 (29)
O(5)	2054 (7)	8645 (4)	7963 (3)	83 (16)	C(2)	2154 (15)	7640 (11)	6069 (7)	535 (47)
O(6)	1480 (8)	10178 (4)	8457 (3)	128 (19)	C(3)	3039 (16)	7262 (12)	6411 (7)	644 (55)
O(7)	6392 (8)	10293 (5)	10002 (4)	151 (19)	N(4)	2539 (9)	6401 (6)	6665 (4)	238 (23)
O(8)	−1471 (8)	9650 (5)	10000 (4)	145 (18)	N(11)	7228 (11)	6149 (8)	5866 (5)	355 (29)
O(9)	6970 (9)	8747 (6)	10487 (4)	225 (21)	C(13)	7372 (20)	4709 (10)	5336 (8)	671 (54)
O(10)	−1433 (8)	9680 (5)	5954 (4)	171 (20)	C(12)	7804 (15)	5684 (10)	5465 (6)	450 (41)
O(11)	7955 (9)	11252 (5)	10459 (4)	216 (21)	N(14)	7666 (19)	4017 (11)	5699 (7)	832 (56)
O(12)	6476 (8)	10304 (5)	5947 (4)	147 (19)	N(21)	7129 (13)	8976 (9)	1674 (6)	498 (36)
O(13)	5613 (8)	7606 (5)	7150 (3)	199 (19)	C(22)	7770 (19)	9552 (11)	2005 (8)	745 (62)
O(14)	3517 (7)	7670 (5)	7425 (3)	201 (20)	C(23)	7375 (24)	10573 (12)	2076 (9)	919 (76)
O(15)	4853 (8)	9164 (5)	6867 (3)	165 (18)	N(24)	7795 (16)	11155 (11)	1667 (7)	738 (49)
O(16)	5351 (7)	8741 (5)	7907 (3)	196 (18)	N(31)	822 (8)	12398 (6)	6248 (4)	186 (21)
O(17)	4221 (8)	10558 (5)	6279 (3)	152 (18)	C(32)	1965 (13)	12702 (12)	6404 (7)	569 (50)
O(18)	2548 (7)	9800 (5)	6681 (4)	222 (19)	C(33)	2801 (14)	12291 (14)	6059 (8)	699 (58)
O(19)	4226 (7)	11239 (5)	7125 (3)	103 (17)	N(34)	3880 (9)	12474 (8)	6293 (5)	315 (27)
O(20)	−596 (8)	12221 (5)	7198 (3)	188 (19)	O(100)	8952 (16)	7392 (12)	6194 (8)	1030 (55)
O(21)	−435 (8)	10912 (5)	7875 (3)	178 (19)	O(200)	3475 (16)	7557 (13)	8745 (9)	1072 (56)

the compound loses its crystallinity even before the decomposition of the template is complete.

Crystal and experimental data for the structural characterization of the as-synthesized compound are given in Table I. X-ray measurements were made using an Enraf-Nonius FAST TV area detector and graphite-monochromated Mo Kα radiation from a rotating anode generator. Intensity data corresponding to one hemisphere of reciprocal space were collected using two ω scan ranges of 100° with a ϕ shift of 90° (to achieve >180° in total) at $\chi = 0°$, followed by two further ω rotations of 70° with a ϕ shift of 90° at $\chi = 90°$, to record the missing cusp data. The detector swing angle was 20° and the crystal-to-detector distance 50 mm, so as to give all possible data to $\theta_{max} = 22.35°$.

Of the reflections scanned, 16 592 satisfied the conditions for acceptable measurement and were merged to give 6422 unique data (Friedel's law not assumed) of which 4104 were considered to be observed $F > 3\sigma(F)$. The structure was solved by direct methods[11] and refined by full-matrix least squares[12] to $R = 0.035$ and $R_w = 0.041$. An empirical absorption correction was applied at the isotropic refinment stage (DIFABS).[13] It was possible to locate the charge-balancing template organic cations and two extraframework water molecules (O(100) and O(200)). In the final difference Fourier map, the largest peak was 1.8 e Å^{-3} in the vicinity of one of the template ions. Organic H atoms were geometrically placed, and restraints[14,15] were applied to the organic template species. A total of 403 least-squares parameters were used. During the final stages of refinement a Chebychev weighting scheme with coefficients of 17.097, −9.818, 13.285 was applied.[16] The absolute structure was determined by Flack's[17] method. The value of the enantiopole (0.993 (27)) showed that the wrong absolute structure had been chosen and the coordinates were accordingly inverted. Complex neutral atom scattering factors were taken from the ref 18.

Results and Discussion

Atomic parameters, bond lengths and angles are given in Table II–IV, respectively. Selected interatomic contacts related to hydrogen bonding within the compound are listed in Table V.

The asymmetrical units contains 18 Ge atoms which have three different coordination numbers. Two of the Ge atoms are coordinated by six O atoms so as to give a reasonable octahedron in which the Ge–O bond lengths (1.869–1.915 Å) are comparable to those found in the rutile form of GeO_2[19] (Ge–O: 1.868–1.911 Å). Eight Ge atoms are bonded to five O atoms to give distorted trigonal bipyramids (tbp). The axial Ge–O bond lengths fall into two sets: those involving triply bonding oxygen atoms (see

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Table III. Interatomic Distances (Angstroms) with Esds in Parentheses[a]

Ge(1)–O(1)	1.890 (9)	Ge(10)–O(32)	1.831 (8)
Ge(1)–O(2)	1.877 (9)	Ge(10)–O(36)	1.759 (8)
Ge(1)–O(3)	1.915 (9)	Ge(10)–O(37)	1.811 (8)
Ge(1)–O(4)	1.902 (6)	Ge(10)–O(38)	1.767 (9)
Ge(1)–O(5)	1.869 (7)	Ge(11)–O(3)	1.758 (9)
Ge(1)–O(6)	1.886 (9)	Ge(11)–O(16)	1.764 (8)
Ge(2)–O(7)	1.914 (10)	Ge(11)–O(26)	1.712 (10)
Ge(2)–O(8)	1.909 (10)	Ge(11)–O(39)	1.758 (7)
Ge(2)–O(9)	1.887 (8)	Ge(12)–O(4)	1.735 (8)
Ge(2)–O(10)	1.891 (10)	Ge(12)–O(13)	1.721 (7)
Ge(2)–O(11)	1.874 (8)	Ge(12)–O(19)	1.739 (8)
Ge(2)–O(12)	1.874 (10)	Ge(12)–O(39)	1.807 (9)
Ge(3)–O(2)	2.101 (7)	Ge(13)–O(5)	1.766 (8)
Ge(3)–O(13)	1.807 (8)	Ge(13)–O(20)	1.720 (7)
Ge(3)–O(14)	1.766 (8)	Ge(13)–O(25)	1.734 (9)
Ge(3)–O(15)	1.763 (8)	Ge(13)–O(40)	1.788 (8)
Ge(3)–O(16)	1.755 (9)	Ge(14)–O(6)	1.739 (9)
Ge(4)–O(2)	1.945 (9)	Ge(14)–O(21)	1.770 (8)
Ge(4)–O(15)	1.797 (8)	Ge(14)–O(30)	1.703 (10)
Ge(4)–O(17)	1.849 (9)	Ge(14)–O(40)	1.772 (7)
Ge(4)–O(18)	1.754 (9)	Ge(15)–O(9)	1.737 (11)
Ge(4)–O(19)	1.799 (7)	Ge(15)–O(28)	1.768 (9)
Ge(5)–O(1)	2.012 (8)	Ge(15)–O(37)	1.747 (7)
Ge(5)–O(20)	1.849 (8)	Ge(15)–O(41)	1.753 (9)
Ge(5)–O(21)	1.779 (9)	Ge(16)–O(10)	1.721 (10)
Ge(5)–O(22)	1.780 (9)	Ge(16)–O(24)	1.718 (9)
Ge(5)–O(23)	1.740 (9)	Ge(16)–O(33)	1.739 (8)
Ge(6)–O(1)	1.958 (9)	Ge(16)–O(41)	1.788 (8)
Ge(6)–O(18)	1.749 (9)	Ge(17)–O(11)	1.736 (11)
Ge(6)–O(22)	1.815 (8)	Ge(17)–O(31)	1.769 (9)
Ge(6)–O(24)	1.828 (9)	Ge(17)–O(34)	1.735 (7)
Ge(6)–O(25)	1.795 (7)	Ge(17)–O(42)	1.769 (9)
Ge(7)–O(7)	1.907 (10)	Ge(18)–O(12)	1.720 (10)
Ge(7)–O(26)	1.820 (10)	Ge(18)–O(17)	1.724 (9)
Ge(7)–O(27)	1.752 (9)	Ge(18)–O(36)	1.752 (8)
Ge(7)–O(28)	1.779 (8)	Ge(18)–O(42)	1.787 (7)
Ge(7)–O(29)	1.783 (7)	N(1)–C(2)	1.46*
Ge(8)–O(8)	1.903 (10)	C(2)–C(3)	1.53*
Ge(8)–O(27)	1.774 (8)	C(3)–N(4)	1.54*
Ge(8)–O(30)	1.824 (10)	N(11)–C(12)	1.47*
Ge(8)–O(31)	1.768 (8)	C(13)–C(12)	1.53*
Ge(8)–O(32)	1.783 (8)	C(13)–N(14)	1.46*
Ge(9)–O(7)	2.106 (8)	N(21)–C(22)	1.46*
Ge(9)–O(29)	1.796 (8)	C(22)–C(23)	1.54*
Ge(9)–O(33)	1.774 (9)	C(23)–N(24)	1.50*
Ge(9)–O(34)	1.797 (8)	N(31)–C(32)	1.52*
Ge(9)–O(35)	1.729 (9)	C(32)–C(33)	1.52*
Ge(10)–O(8)	2.047 (8)	C(33)–N(34)	1.48*

[a] An asterisk denotes that a restraint was applied to the bond.

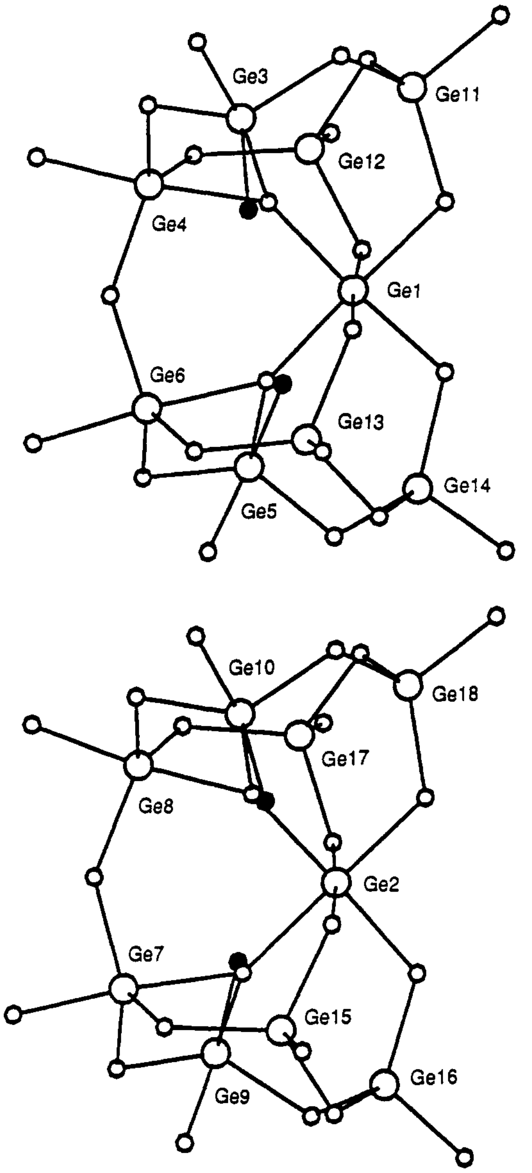

Figure 1. The two crystallographically independent building blocks (top) containing Ge1, Ge3–6, Ge11–14 and (bottom) containing Ge2, Ge7–10, Ge15–18 in the microporous framework. Ge11–18 each are 4-, Ge3–10 each are 5-, and Ge1,2 each are 6-coordinated. The hydroxyl oxygen atoms are shaded.

below) have a relatively large spread of values (1.903–2.106 Å), while those oxygen atoms that are bonded only to two germanium atoms have Ge–O distances between 1.797 and 1.849 Å. The remaining eight Ge atoms have distorted tetrahedral coordination geometry (Ge–O, 1.703–1.807 Å; O–Ge–O, 96.4–119.1°). These polyhedra are then linked to give rise to the common building block upon which the structure is constructed. The two crystallographically independent building blocks are illustrated in Figure 1. The building block is essentially a highly distorted body-centered cube of Ge atoms. The body-centered Ge atom is linked via bridging oxygen atoms to all the cube vertexes. There are Ge–O–Ge links between the Ge atoms which constitute the relatively undistorted face of the cube, e.g., between Ge(3) and Ge(4), but only one Ge–O–Ge linkage across the tetragonally elongated edge of the cube, e.g., Ge(4) and Ge(6). The effect of this is to "tip" the undistorted faces of the cube away from each other. The vertices of the "cube" building block are then shared to give rise to the microporous structure.

In the structure there are three types of channels, two of which have the same ring aperture. The smaller one has an eight-membered ring and runs along [100] (Figure 2, top) with an effective free diameter of 2.3–2.8 Å. Intersecting this channel are the two with an oval 10-membered window (Figure 2, bottom), which has a free diameter varying between 2.7 and 5.2 Å.

We believe the formula of the framework to be $[Ge_{18}O_{38}(OH)_4]^{8-}$. This implies that the template molecules are diprotonated though we cannot rule out the possibility that some of the water molecules are protonated to hydroxonium ions.

Chemically there are three distinct types of O atoms in the framework structure. The most numerous are two-coordinated bridging O atoms with a large spread in both the observed Ge–O bond length (1.703–1.915 Å) and the Ge–O–Ge bond angle (106.9–142.3°). The second type of framework oxygen present are four hydroxyl groups attached in the equatorial plane of the tbp Ge atoms. The observed Ge–O distances (av 1.750 Å) are comparable to singly bridging O atoms which also lie in the equatorial plane of tbp Ge atoms (av 1.779 Å) and thus clearly indicate the necessity of attaching hydrogen atoms to these O atoms on the grounds of elementary valence consider-

Table IV. Bond Angles (Degrees) with Esds in Parentheses[a]

O(2)–Ge(1)–O(1)	95.6 (5)	O(22)–Ge(5)–O(1)	79.7 (4)	O(38)–Ge(10)–O(9)	92.9 (4)	Ge(6)–O(1)–Ge(1)	129.7 (4)
O(3)–Ge(1)–O(1)	176.4 (4)	O(22)–Ge(5)–O(20)	87.2 (4)	O(38)–Ge(10)–O(32)	129.0 (4)	Ge(6)–O(1)–Ge(5)	93.2 (4)
O(3)–Ge(1)–O(2)	87.5 (4)	O(22)–Ge(5)–O(21)	116.6 (4)	O(38)–Ge(10)–O(36)	111.7 (4)	Ge(3)–O(2)–Ge(1)	135.9 (4)
O(4)–Ge(1)–O(1)	88.7 (3)	O(23)–Ge(5)–O(1)	93.4 (4)	O(38)–Ge(10)–O(37)	96.6 (4)	Ge(4)–O(2)–Ge(1)	130.0 (4)
O(4)–Ge(1)–O(2)	91.6 (3)	O(23)–Ge(5)–O(20)	96.1 (4)	O(16)–Ge(11)–O(3)	113.4 (4)	Ge(4)–O(2)–Ge(3)	90.7 (4)
O(4)–Ge(1)–O(3)	89.3 (3)	O(23)–Ge(5)–O(21)	118.1 (4)	O(26)–Ge(11)–O(3)	110.1 (5)	Ge(11)–O(3)–Ge(1)	114.4 (5)
O(5)–Ge(1)–O(1)	93.0 (3)	O(23)–Ge(5)–O(22)	124.7 (4)	O(26)–Ge(11)–O(16)	99.1 (4)	Ge(12)–O(4)–Ge(1)	115.6 (4)
O(5)–Ge(1)–O(2)	90.2 (3)	O(18)–Ge(6)–O(1)	95.4 (4)	O(39)–Ge(11)–O(3)	113.1 (4)	Ge(13)–O(5)–Ge(1)	116.9 (4)
O(5)–Ge(1)–O(3)	88.8 (3)	O(22)–Ge(6)–O(1)	80.4 (4)	O(39)–Ge(11)–O(16)	111.5 (4)	Ge(14)–O(6)–Ge(1)	118.4 (5)
O(5)–Ge(1)–O(4)	177.4 (4)	O(22)–Ge(6)–O(18)	119.9 (4)	O(39)–Ge(11)–O(26)	108.7 (4)	Ge(7)–O(7)–Ge(2)	133.0 (5)
O(6)–Ge(1)–O(1)	88.7 (4)	O(24)–Ge(6)–O(1)	174.2 (3)	O(13)–Ge(12)–O(4)	102.7 (4)	Ge(9)–O(7)–Ge(2)	132.8 (4)
O(6)–Ge(1)–O(2)	175.5 (4)	O(24)–Ge(6)–O(18)	88.1 (5)	O(19)–Ge(12)–O(4)	113.0 (4)	Ge(9)–O(7)–Ge(7)	91.5 (4)
O(6)–Ge(1)–O(3)	88.2 (4)	O(24)–Ge(6)–O(22)	93.9 (4)	O(19)–Ge(12)–O(13)	108.7 (4)	Ge(8)–O(8)–Ge(2)	132.1 (4)
O(6)–Ge(1)–O(4)	87.4 (3)	O(25)–Ge(6)–O(1)	91.0 (4)	O(39)–Ge(12)–O(4)	107.8 (4)	Ge(10)–O(8)–Ge(2)	132.7 (5)
O(6)–Ge(1)–O(5)	90.7 (3)	O(25)–Ge(6)–O(18)	119.8 (4)	O(39)–Ge(12)–O(13)	110.2 (4)	Ge(10)–O(8)–Ge(8)	94.5 (4)
O(8)–Ge(2)–O(7)	92.0 (5)	O(25)–Ge(6)–O(22)	120.2 (4)	O(39)–Ge(12)–O(19)	113.8 (4)	Ge(15)–O(9)–Ge(2)	115.2 (5)
O(9)–Ge(2)–O(7)	89.4 (4)	O(25)–Ge(6)–O(24)	91.3 (4)	O(20)–Ge(13)–O(5)	102.9 (4)	Ge(16)–O(10)–Ge(2)	118.1 (6)
O(9)–Ge(2)–O(8)	88.9 (4)	O(26)–Ge(7)–O(7)	175.2 (4)	O(25)–Ge(13)–O(5)	113.3 (4)	Ge(17)–O(11)–Ge(2)	117.9 (5)
O(10)–Ge(2)–O(7)	88.4 (4)	O(27)–Ge(7)–O(7)	94.1 (4)	O(25)–Ge(13)–O(20)	110.2 (4)	Ge(18)–O(12)–Ge(2)	120.2 (5)
O(10)–Ge(2)–O(8)	178.8 (3)	O(27)–Ge(7)–O(26)	90.6 (5)	O(40)–Ge(13)–O(5)	106.7 (4)	Ge(12)–O(13)–Ge(3)	131.6 (5)
O(10)–Ge(2)–O(9)	90.0 (4)	O(28)–Ge(7)–O(7)	90.3 (4)	O(40)–Ge(13)–O(20)	108.2 (4)	Ge(4)–O(15)–Ge(3)	108.1 (5)
O(11)–Ge(2)–O(7)	89.2 (4)	O(28)–Ge(7)–O(26)	88.0 (4)	O(40)–Ge(13)–O(25)	114.8 (4)	Ge(11)–O(16)–Ge(3)	122.6 (5)
O(11)–Ge(2)–O(8)	91.2 (4)	O(28)–Ge(7)–O(27)	124.5 (4)	O(21)–Ge(14)–O(6)	118.8 (4)	Ge(18)–O(17)–Ge(4)	138.7 (5)
O(11)–Ge(2)–O(9)	178.7 (4)	O(29)–Ge(7)–O(7)	83.1 (4)	O(30)–Ge(14)–O(6)	110.1 (5)	Ge(6)–O(18)–Ge(4)	141.7 (6)
O(11)–Ge(2)–O(10)	89.9 (4)	O(29)–Ge(7)–O(26)	93.8 (4)	O(30)–Ge(14)–O(21)	98.2 (4)	Ge(12)–O(19)–Ge(4)	120.4 (4)
O(12)–Ge(2)–O(7)	178.9 (4)	O(29)–Ge(7)–O(27)	115.4 (3)	O(40)–Ge(14)–O(6)	108.9 (3)	Ge(13)–O(20)–Ge(5)	132.6 (5)
O(12)–Ge(2)–O(8)	88.5 (4)	O(29)–Ge(7)–O(28)	120.0 (4)	O(40)–Ge(14)–O(21)	105.5 (4)	Ge(14)–O(21)–Ge(5)	120.9 (5)
O(12)–Ge(2)–O(9)	89.6 (4)	O(27)–Ge(8)–O(8)	95.7 (4)	O(40)–Ge(14)–O(30)	115.3 (4)	Ge(6)–O(22)–Ge(5)	106.7 (5)
O(12)–Ge(2)–O(10)	91.1 (5)	O(30)–Ge(8)–O(8)	172.1 (4)	O(28)–Ge(15)–O(9)	112.0 (5)	Ge(16)–O(24)–Ge(6)	140.3 (5)
O(12)–Ge(2)–O(11)	91.7 (4)	O(30)–Ge(8)–O(27)	89.8 (5)	O(37)–Ge(15)–O(9)	103.4 (4)	Ge(13)–O(25)–Ge(6)	123.0 (5)
O(13)–Ge(3)–O(2)	168.1 (4)	O(31)–Ge(8)–O(8)	93.4 (4)	O(37)–Ge(15)–O(28)	108.9 (4)	Ge(11)–O(26)–Ge(7)	142.3 (5)
O(14)–Ge(3)–O(2)	91.9 (3)	O(31)–Ge(8)–O(27)	117.5 (4)	O(41)–Ge(15)–O(9)	109.5 (4)	Ge(8)–O(27)–Ge(7)	140.5 (6)
O(14)–Ge(3)–O(13)	96.1 (4)	O(31)–Ge(8)–O(30)	89.0 (4)	O(41)–Ge(15)–O(28)	115.7 (4)	Ge(15)–O(28)–Ge(7)	119.1 (4)
O(15)–Ge(3)–O(2)	78.1 (4)	O(32)–Ge(8)–O(8)	81.8 (4)	O(41)–Ge(15)–O(37)	106.6 (4)	Ge(9)–O(29)–Ge(7)	107.0 (4)
O(15)–Ge(3)–O(13)	90.1 (4)	O(32)–Ge(8)–O(27)	120.3 (3)	O(24)–Ge(16)–O(10)	113.7 (5)	Ge(14)–O(30)–Ge(8)	141.5 (5)
O(15)–Ge(3)–O(14)	122.4 (4)	O(32)–Ge(8)–O(30)	90.5 (4)	O(33)–Ge(16)–O(10)	115.9 (4)	Ge(17)–O(31)–Ge(8)	121.1 (5)
O(16)–Ge(3)–O(2)	86.7 (4)	O(32)–Ge(8)–O(31)	122.2 (4)	O(33)–Ge(16)–O(24)	96.4 (4)	Ge(10)–O(32)–Ge(8)	106.9 (4)
O(16)–Ge(3)–O(13)	97.3 (4)	O(29)–Ge(9)–O(7)	77.3 (4)	O(41)–Ge(16)–O(10)	110.5 (4)	Ge(16)–O(33)–Ge(9)	122.1 (5)
O(16)–Ge(3)–O(14)	117.6 (4)	O(33)–Ge(9)–O(7)	88.9 (4)	O(41)–Ge(16)–O(24)	111.9 (4)	Ge(17)–O(34)–Ge(9)	132.3 (5)
O(16)–Ge(3)–O(15)	118.2 (4)	O(33)–Ge(9)–O(29)	119.1 (4)	O(41)–Ge(16)–O(33)	107.7 (4)	Ge(18)–O(36)–Ge(10)	121.9 (5)
O(15)–Ge(4)–O(2)	81.6 (4)	O(34)–Ge(9)–O(7)	165.5 (4)	O(31)–Ge(17)–O(11)	110.7 (5)	Ge(15)–O(37)–Ge(10)	134.8 (5)
O(17)–Ge(4)–O(2)	175.4 (4)	O(34)–Ge(9)–O(29)	88.3 (4)	O(34)–Ge(17)–O(11)	103.3 (4)	Ge(12)–O(39)–Ge(11)	118.2 (5)
O(17)–Ge(4)–O(15)	94.8 (4)	O(34)–Ge(9)–O(33)	97.3 (4)	O(34)–Ge(17)–O(31)	111.8 (4)	Ge(14)–O(40)–Ge(13)	118.1 (4)
O(18)–Ge(4)–O(2)	93.8 (4)	O(35)–Ge(9)–O(7)	91.9 (4)	O(42)–Ge(17)–O(11)	111.4 (4)	Ge(16)–O(41)–Ge(15)	119.3 (5)
O(18)–Ge(4)–O(15)	114.4 (4)	O(35)–Ge(9)–O(29)	125.5 (4)	O(42)–Ge(17)–O(31)	109.8 (4)	Ge(18)–O(42)–Ge(17)	119.4 (5)
O(18)–Ge(4)–O(17)	90.4 (4)	O(35)–Ge(9)–O(33)	113.9 (4)	O(42)–Ge(17)–O(34)	109.7 (4)	C(3)–C(2)–N(1)	104.2*
O(19)–Ge(4)–O(2)	90.7 (3)	O(35)–Ge(9)–O(34)	97.4 (4)	O(17)–Ge(18)–O(12)	115.4 (5)	N(4)–C(3)–C(2)	106.7*
O(19)–Ge(4)–O(15)	121.2 (4)	O(32)–Ge(10)–O(8)	76.8 (4)	O(36)–Ge(18)–O(12)	114.2 (4)	N(14)–C(13)–C(12)	111.5*
O(19)–Ge(4)–O(17)	88.6 (3)	O(36)–Ge(10)–O(8)	91.2 (4)	O(36)–Ge(18)–O(17)	97.9 (4)	C(13)–C(12)–N(11)	115.0*
O(19)–Ge(4)–O(18)	124.3 (4)	O(26)–Ge(10)–O(32)	118.3 (4)	O(42)–Ge(18)–O(12)	110.5 (4)	C(23)–C(22)–N(21)	116.4*
O(20)–Ge(5)–O(1)	166.7 (4)	O(37)–Ge(10)–O(8)	162.2 (4)	O(42)–Ge(18)–O(17)	110.7 (4)	N(24)–C(23)–C(22)	108.5*
O(21)–Ge(5)–O(1)	89.5 (4)	O(37)–Ge(10)–O(32)	85.6 (3)	O(42)–Ge(18)–O(36)	107.3 (4)	C(33)–C(32)–N(31)	108.7*
O(21)–Ge(5)–O(20)	94.2 (4)	O(37)–Ge(10)–O(36)	99.1 (4)	Ge(5)–O(1)–Ge(1)	136.3 (5)	N(34)–C(33)–C(32)	104.1*

[a] An asterisk denotes that a restraint was applied to atoms involving in this bond.

Table V. Selected Interatomic Distances Related to Hydrogen Bonds (Å) with Esds in Parentheses

O(14)–O(2)	2.789 (9)	O(35)–O(7)	2.769 (9)
O(23)–O(1)	2.737 (9)	O(38)–O(8)	2.771 (10)

ations alone. More quantitatively a bond valence calculation[19] shows valences ranging between 0.950 and 1.053 vu (valence unit) when no consideration is made for H atoms. That one hydrogen atom should be attached (and not two hydrogen atoms if the oxygen atom was a water molecule) can be rationalized if potential hydrogen bonding is taken into account. The strongest hydrogen bonds involving these hydroxyl groups are to O atoms which are coordinated to three Ge atoms (O—O, 2.737–2.789 Å). Bond valence calculations[20] for these triply bridging O atoms show values between 1.669 to 1.751 vu, while the O—O separations indicate a contribution of ca. 0.2 vu to the oxygen atom which is acting as an acceptor in the hydrogen bond and 0.8 vu to the donor O atom. These are the order required to satisfy the valences of the respective O atoms if the tbp O atoms are part of hydroxyl groups and the triply bridging O atoms are not directly bonded to H atoms.

The final type of oxygen atom in the structure is the triply bridging O atoms. Bond valence calculations show that these O atoms are not hydroxyl groups (see above). This can be contrasted to the situation in $GaPO_4$-14[21] and $AlPO_4$-15[22] where O atoms which triply bridge three Ga(Al) atoms are thought to be hydroxyl groups. Triply bridging O atoms have also been observed in several other cases, e.g., $GaPO_4$-12,[23] a layered gallium phosphate,[24] and a layered manganese phosphate.[25] However in these cases

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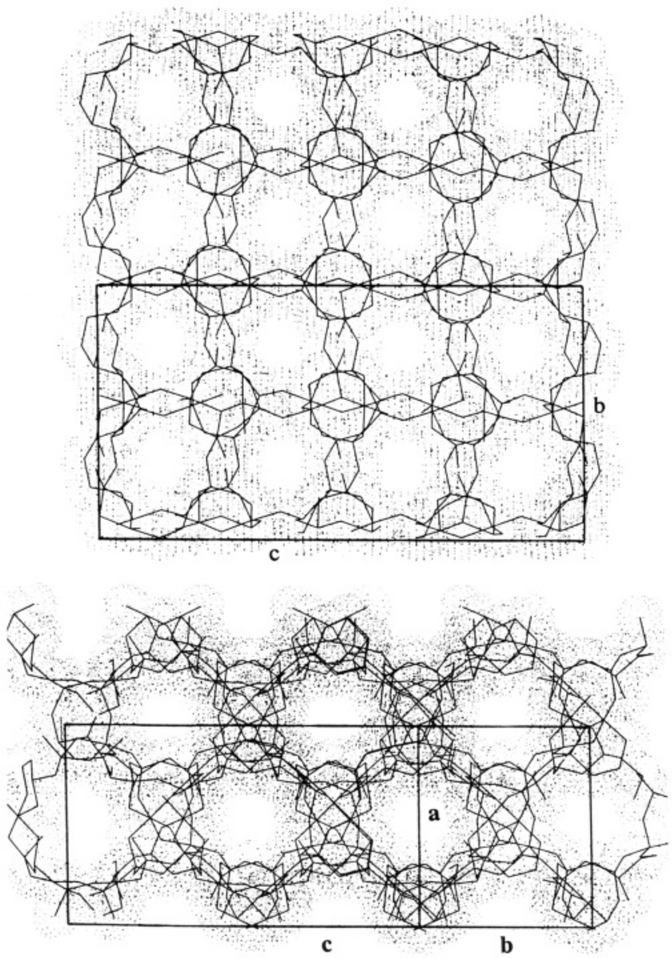

Figure 2. Projections of the structure of the $[Ge_{18}O_{38}(OH)_4]^{8-}$ microporous anion viewed along (top) [100] and (bottom) [012] or [012]. For simplicity only the framework connections are shown. Each straight line denotes a Ge–O bond and the van der Waals networks are represented by the fine dots.

the O atoms bridge a heteronuclear arrangement of atoms viz. two Ga and one P or two Mn and one P atoms.

In this new material with a three-dimensional microporous framework, the Ge atoms, i.e., the non-oxygen framework species are not only four- but also five- and six-coordinated. This expansion in coordination number in proceeding from silicon to germanium is to be expected for post-transition elements of group 14 and is reflected by the fact that of the many polymorphs of pure SiO_2, only the rare mineral stishovite (rutile structure)[19,26,27] contains the silicon in 6-fold coordination. Of the crystalline polymorphs of GeO_2, on the other hand, the so-called insoluble rutile form can be straightforwardly obtained from the quartz variety.[28] This expansion of coordination number may be utilized in the future in making new microporous solids in which there are novel building units.

We have carried out some preliminary computational assessments of the stability of microporous germanium-rich silicates as well as the GeO_2 end member form of silicalite I.[29] It transpires that, thermodynamically, these solids are about as stable as those of their silica-rich structural analogues.

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Registry No. GeO_2, 1310-53-8; en, 107-15-3; $[Ge_{18}O_{38}(OH)_4]^{8-}[C_2N_2H_{10}]_4{}^{2+}\cdot 2H_2O$, 141958-37-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates for the title compound (2 pages); table of calculated and observed structure factors (20 pages). Ordering information is given on any masthead page.

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