Synthesis, Structure and Characterization of a Novel Germanium Dioxide with Occluded Tetramethylammonium Hydroxide†

Jun Cheng, Ruren Xu* and Guangdi Yang
Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

A crystalline microporous germanate has been discovered. This novel material is based on a germanium dioxide framework and was synthesised hydrothermally at 180 °C in the presence of NMe_4OH as templating agent. A single-crystal X-ray study of the compound revealed a monoclinic germanium dioxide clathrate with space group $P2_1/n$ and unit cell parameters $a = 9.690(4)$, $b = 9.231(5)$, $c = 18.019(8)$ Å, $\beta = 98.46(4)°$, $Z = 4$, $R = 0.0417$ and $R' = 0.0434$. The compound has a framework consisting of GeO_4 tetrahedrons and GeO_5 trigonal bipyramids which form four-, six- and eight-membered ring channels along the *c* axis. The cation NMe_4^+ is located in the six-membered ring channel and is a key factor in the formation and stability of the framework.

A major scientific and technological achievement since 1949 has been the discovery and the development of synthetic crystalline aluminosilicate zeolite, as molecular sieve absorbents and catalysts. Over the last decade a series of microporous aluminophosphates[1] and silica molecular sieves[2] have been prepared and extensively studied, followed by the syntheses of many microporous gallophosphates[3] and a new family of microporous metal sulphides.[4]

Of all the zeolitic materials, silica molecular sieves and clathrates are of importance because of their novel structures, high thermal and hydrothermal stabilities and some practical applications as absorbents, catalysts, *etc.* More than 10 kinds of silica molecular sieves and clathrates have been hydrothermally synthesised with amines or quaternary ammoniums as structure-directing agents. Like Si, Ge tends to surround itself with an oxygen tetrahedron which may join to larger units through shared corners. This similarity of Ge and Si is underlined by the fact that some compounds of the two elements have proved to be isomorphous. However, so far, all the crystals reported based on a germanium dioxide framework are not associated with amines and quaternary ammoniums. So it is an extremely attractive question whether the germanium dioxide framework is able to occlude amines or quaternary ammoniums. In this paper, we present the synthesis, structure and characterization of a novel framework germanium dioxide inclusion compound which was first synthesised by using NMe_4OH as the template.

Experimental

Synthesis.—Germanium dioxide, NMe_4OH and water were mixed in the molar ratio of 1:0.6:30 and stirred until homogeneous. The reaction was allowed to proceed under hydrothermal (static) conditions in a poly(tetrafluoroethylene)-coated stainless-steel autoclave at 180 °C for 14 d. After crystallization, the crystalline product was filtered off, washed with distilled water, dried at ambient temperature and then characterized by means of chemical analysis, X-ray powder diffraction, IR spectrometry and thermal analysis.

Following the same synthetic procedure in the presence of some ethylene glycol, well grown single crystals were obtained of approximate size 75 × 75 × 150 μm which were suitable for single-crystal X-ray study.

Crystal Structure Determination.—*Crystal data.* $Ge_6O_{12}\cdot NMe_4OH$, $M = 718.66$, monoclinic, space group $P2_1/n$, $a = 9.690(4)$, $b = 9.231(5)$, $c = 18.019(8)$ Å, $\beta = 98.46(4)°$, $D_c = 2.99$ g cm^{-3}, $Z = 4$, $U = 1594.23$ Å^3, $F(000) = 399.87$, μ(Mo-Kα) = 20.00 cm^{-1}.

The intensity data were collected on a Nicolet XRD R3 diffractometer for a crystal with dimensions 0.075 × 0.075 × 0.150 mm within the range $3 < 2\theta < 50°$, using a graphite monochromator, Mo-Kα radiation ($\lambda = 0.710\,69$ Å) and ω scans with variable speed. The structure was solved by direct methods on the basis of 759 unique reflections [$I \geqslant 3.5\sigma(I)$] out of 2913 measured. An absorption correction was applied. All computations were carried out on a NOVA-4 minicomputer by using the SHELXTL program system[5]; and a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.0006\ F^2]$ was applied. The structure refinements, anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms, converged to the final *R* and *R′* values of 0.0417 and 0.0434, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Description of the Structure.—Atomic coordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3. The crystal is constructed from a germanium dioxide framework. The composition analysis of the sample corresponds to the asymmetric unit content of $Ge_6O_{12}\cdot NMe_4OH$ in which five Ge atoms are tetrahedrally co-ordinated and one is co-ordinated by five oxygen atoms (Fig. 1) to form a slightly distorted trigonal bipyramid. In each unit cell there are 24 Ge atoms, 48 O atoms and 4 NMe_4OH molecules, and each germanium atom shares an oxygen atom with its adjacent germanium atom in the open framework structure. The length of the bond Ge(3)–O(10b), 1.967(7) Å, which is a bit greater than those of all the other Ge–O bonds (average 1.768 Å), suggests that O(10b) represents a hydroxy group.

The three-dimensional framework viewed along *c* axis is shown in Fig. 2. There are four-, six- and eight-membered rings composed of GeO_4 tetrahedra and GeO_5 trigonal bipyramids, and the largest one-dimensional open channel in the framework results from the packing of eight-membered rings along the *c* axis. There is no channel in any other direction.

The cation NMe_4^+, located in the six-membered ring

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† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

channel, was used as the structure-directing agent. Because of the small sizes of such channels and the negative charges of the germanium dioxide framework, we can derive that the NMe_4^+ was also used to balance the charges of the framework and was the key factor in the formation and the stability of the framework.

Other Measurements.—The X-ray powder diffraction pattern of $Ge_6O_{12}{\cdot}NMe_4OH$ was recorded on a D/MAX-III A diffractometer with Cu-Kα radiation. Samples of the compound formed from different reaction mixtures exhibit similar patterns. By comparison with those of the germanates and silica molecular sieves and clathrates known so far, the pattern of our compound is unique and novel.

Table 1 Atomic coordinates (× 10^4) of $Ga_6O_{12}{\cdot}NMe_4OH$

Atom	*x*	*y*	*z*
Ge(1)	2 824(1)	8 898(1)	1 980(1)
Ge(2)	9 519(1)	4 129(1)	6 009(1)
Ge(3)	7 575(1)	5 881(1)	4 695(1)
Ge(4)	2 684(1)	8 306(1)	3 729(1)
Ge(5)	1 933(1)	6 571(1)	727(1)
Ge(6)	4 466(1)	5 502(1)	4 084(1)
O(1)	680(6)	4 384(7)	3 403(3)
O(2)	3 389(6)	8 780(7)	2 928(3)
O(3)	2 331(7)	7 189(6)	1 651(3)
O(4)	1 462(6)	10 160(7)	1 820(3)
O(5)	1 459(6)	5 617(3)	4 870(3)
O(6)	−1 254(6)	6 175(6)	3 988(3)
O(7)	1 114(6)	7 372(7)	3 542(3)
O(8)	2 142(6)	2 320(6)	4 952(3)
O(9)	6 214(6)	5 431(6)	3 953(3)
O(10)	1 142(7)	9 197(6)	362(4)
O(11)	3 963(6)	7 280(6)	4 284(4)
O(12)	2 321(7)	9 813(7)	4 236(4)
O(13)	130(7)	6 289(7)	564(4)
N	2 038(9)	9 132(10)	6 603(5)
C(1)	2 843(18)	7 794(16)	6 760(10)
C(2)	3 045(13)	10 371(13)	6 641(8)
C(3)	1 047(15)	9 351(18)	7 156(8)
C(4)	−3 757(18)	5 899(20)	838(7)

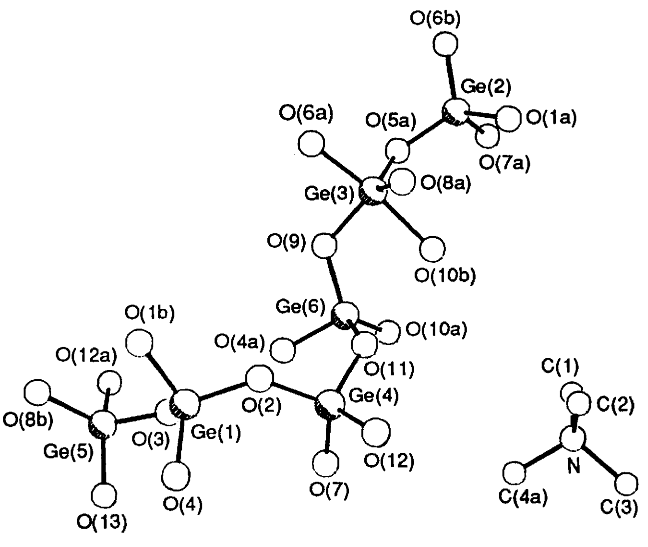

Fig. 1 The asymmetric unit of $Ge_6O_{12}{\cdot}NMe_4OH$

It appears easier to obtain larger crystals of microporous germanates than of microporous silica molecular sieves and clathrasils, but often the crystals which have been grown possess multiply twinned habits or are smaller than those suitable for single-crystal studies. Typical crystal habits displayed by our compound are shown in Fig. 3.

The IR spectrum was recorded on a Nicolet 5DX spectrometer by using a KBr pellet. The characteristic

Table 2 Bond lengths (Å)

Ge(1)–O(2)	1.718(6)	Ge(1)–O(3)	1.728(6)
Ge(1)–O(4)	1.752(6)	Ge(1)–O(1b)	1.754(7)
Ge(2)–O(1a)	1.761(6)	Ge(2)–O(5a)	1.738(6)
Ge(2)–O(6b)	1.703(6)	Ge(2)–O(7a)	1.760(6)
Ge(3)–O(9)	1.785(5)	Ge(3)–O(5a)	1.784(6)
Ge(3)–O(6a)	1.846(6)	Ge(3)–O(8a)	1.785(6)
Ge(3)–O(10b)	1.967)7)	Ge(4)–O(2)	1.742(7)
Ge(4)–O(7)	1.738(6)	Ge(4)–O(11)	1.751(6)
Ge(4)–O(12)	1.728(6)	Ge(5)–O(3)	1.748(6)
Ge(5)–O(13)	1.749(7)	Ge(5)–O(8b)	1.761(6)
Ge(5)–O(12a)	1.773(6)	Ge(6)–O(9)	1.745(6)
Ge(6)–O(11)	1.765(6)	Ge(6)–O(4a)	1.770(5)
Ge(6)–O(10a)	1.722(6)	O(1)–Ge(1a)	1.754(7)
O(1)–Ge(2a)	1.761(6)	O(4)–Ge(6a)	1.770(5)
O(5)–Ge(2a)	1.738(6)	O(5)–Ge(3b)	1.784(6)
O(6)–Ge(2a)	1.703(6)	O(6)–Ge(3a)	1.846(6)
O(7)–Ge(2a)	1.760(6)	O(8)–Ge(3b)	1.784(6)
O(8)–Ge(5a)	1.761(6)	O(10)–Ge(3c)	1.967(7)
O(10)–Ge(6a)	1.722(6)	O(12)–Ge(5b)	1.773(6)
N–C(1)	1.465(18)	N–C(2)	1.498(15)
N–C(3)	1.496(18)	N–C(4a)	1.478(18)

Table 3 Bond angles (°)

O(2)–Ge(1)–O(3)	108.4(3)	O(2)–Ge(1)–O(4)	109.1(3)
O(3)–Ge(1)–O(4)	112.8(3)	O(2)–Ge(1)–O(1b)	104.3(3)
O(3)–Ge(1)–O(1b)	107.5(3)	O(4)–Ge(1)–O(1b)	114.3(3)
O(9)–Ge(3)–O(5a)	115.5(3)	O(9)–Ge(3)–O(6a)	88.8(3)
O(9)–Ge(3)–O(8a)	122.8(3)	O(9)–Ge(3)–O(10b)	86.5(3)
O(2)–Ge(4)–O(7)	113.7(3)	O(2)–Ge(4)–O(11)	106.1(3)
O(7)–Ge(4)–O(11)	111.6(3)	O(2)–Ge(4)–O(12)	111.7(3)
O(7)–Ge(4)–O(12)	105.2(3)	O(11)–Ge(4)–O(12)	108.4(3)
O(3)–Ge(5)–O(13)	106.4(3)	O(3)–Ge(5)–O(8b)	118.0(3)
O(13)–Ge(5)–O(8b)	122.7(3)	O(3)–Ge(5)–O(12a)	103.4(3)
O(13)–Ge(5)–O(12a)	105.2(3)	O(9)–Ge(6)–O(11)	111.4(3)
O(9)–Ge(6)–O(4a)	103.9(3)	O(11)–Ge(6)–O(4a)	103.6(3)
O(9)–Ge(6)–O(10a)	118.3(3)	O(11)–Ge(6)–O(10a)	113.8(3)
Ge(1)–O(2)–Ge(4)	137.2(4)	Ge(1)–O(3)–Ge(5)	129.5(4)
Ge(1)–O(4)–Ge(6a)	122.6(3)	Ge(4)–O(7)–Ge(2a)	131.0(3)
Ge(3)–O(9)–Ge(6)	121.0(3)	Ge(4)–O(11)–Ge(6)	125.5(3)
Ge(4)–O(12)–Ge(5b)	130.1(4)		

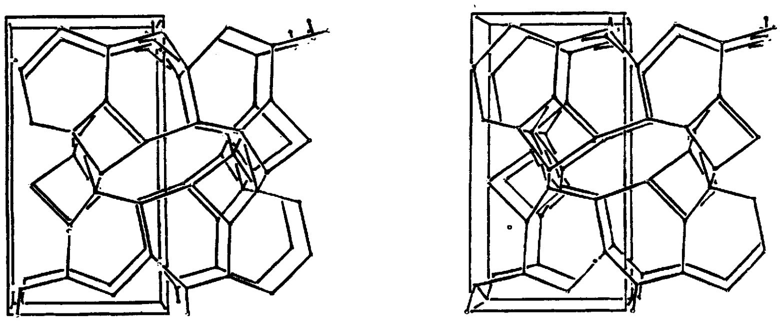

Fig. 2 Stereoview of the $Ge_6O_{12}{\cdot}NMe_4OH$ framework structure along the *c* axis

absorptions are shown in Fig. 4. The bands at 900–700 and 600–500 cm^{-1} are assigned by reference to two more novel germanium dioxide inclusion compounds[6] which were first synthesised in this laboratory and denoted as en–GeO_2 and pd–GeO_2, respectively (en = ethylenediamine, pd = 1,3-propanediamine). By referring to the IR spectra of the Ge-containing zeolites[7] and talcs,[8] we believe that the absorptions of Ge_6O_{12}·NMe_4OH at 837.21 and 567.14 cm^{-1} should be assigned to the internal vibration bands of the framework GeO_4 tetrahedron, the former to the Ge–O asymmetrical stretch and the latter to the Ge–O symmetrical stretch. The IR absorptions of this series of compounds are listed in Table 4. By comparing the ν_{asym} absorption of the dense phase hexagonal GeO_2 with that of Ge_6O_{12}·NMe_4OH we can see that the wavenumber of the latter is about 42 cm^{-1} less than that of the former, which is in accord with the Ge–O bond lengths[8] of the two compounds (Table 4). Furthermore, the different IR spectra of en–GeO_2, pd–GeO_2 and Ge_6O_{12}·NMe_4OH in one respect reveals that these compounds have different framework structures.

The compound has also been subjected to thermal analysis on a Perkin-Elmer DTA instrument in a flow of air at a rate of 10 °C min^{-1} (Fig. 5). In the temperature range 430–481 °C, strong exothermic peaks are seen with a weight loss of about 12.52% of the total amount of the sample. As the temperature increased to 648 °C the total weight loss reached 16.32% which far exceeds the theoretical content of NMe_4OH in the sample, and the colour of the sample turned brown-black. These

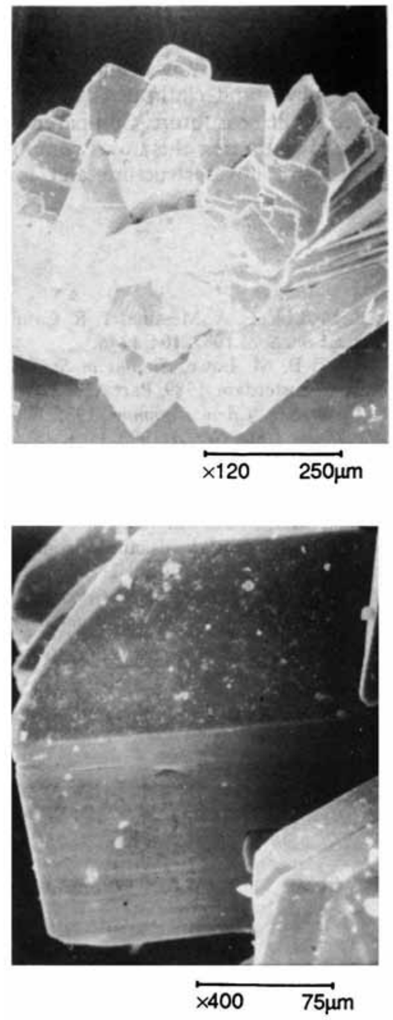

Fig. 3 Scanning electron micrograph of a typical crystal of Ge_6O_{12}·NMe_4OH

Table 4 Main IR absorption bonds (cm^{-1})

Compound	ν_{asym}(Ge–O–Ge)	ν_{sym}(Ge–O–Ge)	Ge–O/Å
Hexagonal GeO_2	879.65	553.64 516.99	1.734–1.741[9]
Ge_6O_{12}·NMe_4OH	837.21	567.14 520.85	1.768 (average)
en–GeO_2	769.70 707.97	580.65 499.63	
pd–GeO_2	775.48	497.70	

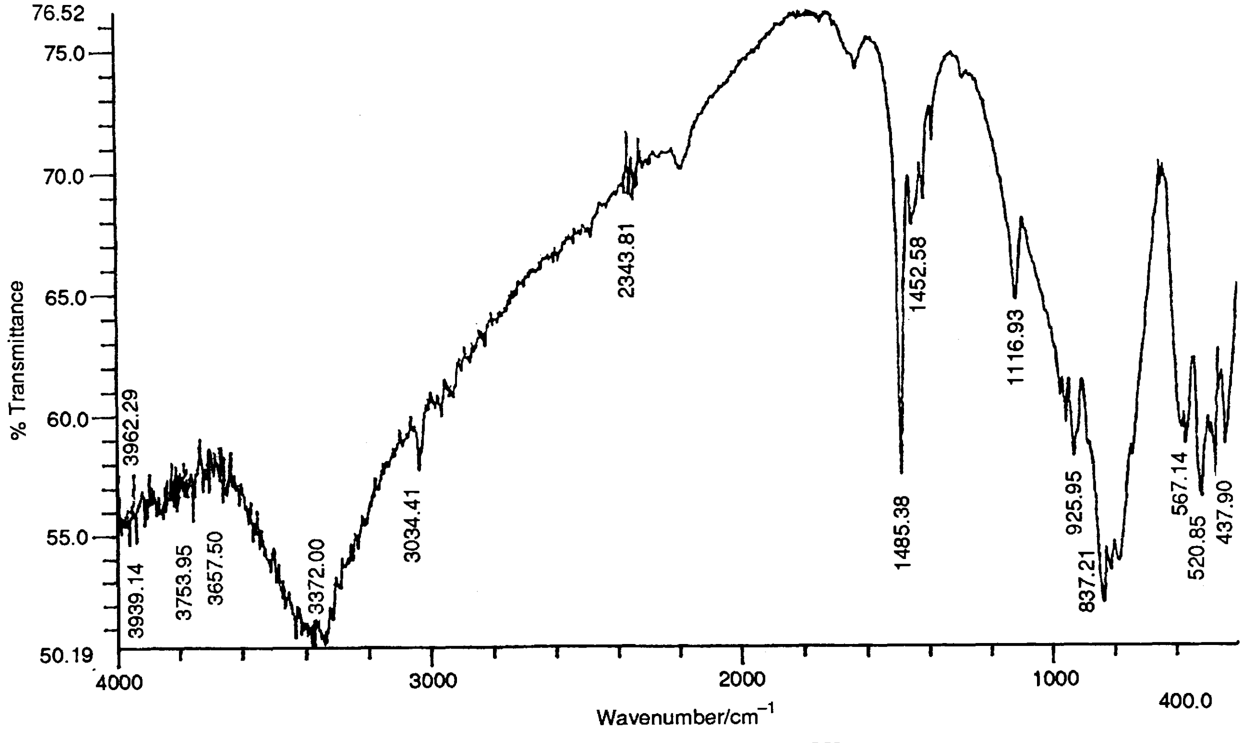

Fig. 4 Infrared spectrum of Ge_6O_{12}·NMe_4OH

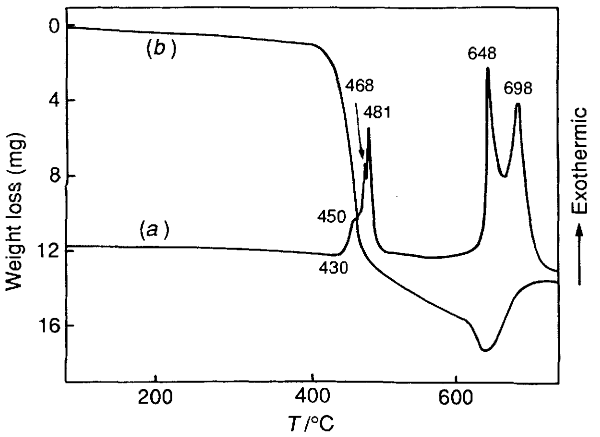

Fig. 5 Differential thermal analysis (*a*) and thermal gravimetry (*b*)

phenomena could be explained if the GeO_2 was reduced to GeO or other low-valent germanium species by NMe_4OH or its decomposition products, accompanied by collapse of the framework. With increasing temperature a part of GeO or low-valent germanium could be oxidized to GeO_2 in the air, accompanied by a large exothermic peak at 648 °C and an increase in weight by about 2%. When the temperature was raised to 698 °C, the other part of the GeO could follow the disproportionation reaction $2GeO \longrightarrow Ge + GeO_2$,[10] accompanied with another exothermic peak (698 °C). These conclusions are supported and confirmed by thermal analysis in a nitrogen atmosphere.

Conclusion

The successful synthesis of the framework germanium dioxide clathrate $Ge_6O_{12}\cdot NMe_4OH$ shows that other germanium dioxide molecular sieves and clathrates are prospective and may be synthesised in the near future. Compared with the silica molecular sieves and clathrates, this novel compound appears to have a unique and novel structure and lower thermal stability.

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Received 21*st September* 1990; *Paper* 0/04295A