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Synthesis, characterization, and properties of the first indium borogermanate incorporating an organic amine ligand: $InBGe_2O_6(OH)_2(CH_3CH(NH_2)CH_2NH_2)\cdot 2H_2O$

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ABSTRACT

A new indium borogermanate incorporating an organic amine ligand, $InBGe_2O_6(OH)_2(CH_3CH(NH_2)CH_2NH_2)\cdot 2H_2O$, was synthesized under solvothermal conditions and characterized by infrared spectroscopy, thermogravimetric analysis, and emission spectroscopy. This compound is a new example of the combination of metal, boron, and germanium atoms into one structure in the presence of organic amine molecules. Its 2D sheets with one 3-, one 4-, and two types of 6-membered rings consist of $In_2O_6N_4$ octahedral dimers, $Ge_2O_6(OH)$ double tetrahedra, and $BO_3(OH)$ groups that are interconnected by water molecules to form a 3D supramolecular framework. Interestingly, the emission spectrum for this compound displays a strong broad band centered at 455 nm.

1. Introduction

Exploration of new crystalline materials has undergone explosive growth since the discovery of aluminosilicates and aluminophosphates [1,2]. These solids not only display interesting structural features, but also have widespread applications in ion exchange, absorption, and catalysis. To seek new materials with different framework topologies and chemical compositions, elements other than Al, P, and Si are introduced into various reaction systems. Thus, a large number of non-aluminosilicate/phosphate-based compounds containing mixed tetrahedral–octahedral units and/or polyatomic structural building groups have been reported [2–5]. Particular interest is associated with germanate frameworks constructed from germanium building units. The flexible coordination behavior (GeO_4, GeO_5, and GeO_6) and larger atomic radius of germanium compared with those of silicon and phosphorus offer more opportunities for the formation of 3-membered rings and cluster units, which is thought to be a key to the synthesis of open-framework structures with large pore sizes or low framework densities [4–5]. Recently, an interesting class of compounds combining both boron and germanium in frameworks with interesting structural features and properties attracted our attention [5]. Following the successful introduction of zinc and indium into germanium frameworks [6], we are now interested in extending our research to the synthesis of amine-templated metal borogermanates. To the best of our knowledge, no example involving the combination of metal, boron, and germanium atoms in one structure in the presence of organic amine molecules has been reported. Herein, we report the first indium borogermanate, $InBGe_2O_6(OH)_2(1,2\text{-DAP})\cdot 2H_2O$ (**1**) [DAP=diaminopropane], incorporating an organic amine ligand. The structure, with one 3-, one 4-, and two types of 6-membered rings, is constructed from $BO_3(OH)$ tetrahedra, $Ge_2O_6(OH)$ double tetrahedra, and $In_2O_6N_4$ octahedral dimers.

2. Experimental section

2.1. Synthesis and characterization

The hydro(solvo)thermal reactions were carried out in Teflon-lined stainless steel Parr acid digestion bombs at 170 °C for 10 d, followed by slow cooling to room temperature at 3 °C/h. Colorless tablet crystals of **1** were obtained by heating a mixture of In$(NO_3)_2\cdot 3H_2O$ (0.3 mmol), HF(aq) (1 mmol, 48% solution), GeO_2 (1 mmol), H_3BO_3 (5 mmol), 1,2-DAP (2 mL), H_2O (1 mL), and pyridine (4 mL). The product contained colorless tablet crystals as the major product and an unidentified white powder.

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Compound **1** was manually separated from the side product, giving a pure sample as judged by comparison of the powder X-ray pattern of **1** with a simulated pattern based on the basic results of single-crystal X-ray diffraction analysis (Fig. S1). Energy-dispersive X-ray fluorescence spectroscopy analysis confirmed the presence of In and Ge in **1**, and the elemental analysis results were consistent with the formula (Anal. Found (calcd): C, 7.01 (7.06); H, 3.01 (3.16); N, 5.45 (5.49)). The infrared spectrum of **1** was recorded by the KBr pellet method. It showed bands characteristic of O–H stretching vibrations at 3423 cm^{-1}, diamine groups at 3260 and 3158 cm^{-1}, BO_4 units at 1048 and 983 cm^{-1}, and GeO_4 groups at 850 and 761 cm^{-1} (Fig. S2). The thermogravimetric analysis of **1** in flowing N_2 at 10 °C min^{-1} showed a weight loss in several overlapping steps between 30 and 970 °C (Fig. S3). Weight losses of 6.83% from 40 to 200 °C, 15.32% from 200 to 540 °C, and 3.82% from 540 to 800 °C were attributed to the loss of two free water molecules (calcd. 7.07%), decomposition of the organic diamine (calcd. 14.53%), and dehydration of the inorganic framework (calcd. 3.53%), respectively. A subsequent large weight loss was assigned to the removal of volatile germanium oxide phases [4f,5d].

2.2. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction: colorless crystals of **1** were selected for indexing and intensity data collection on a Bruker X8 Apex2 CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected in 33778 frames with ω scans (width: 0.10° per frame). Empirical absorption corrections were performed by SADABS program ($T_{\min,\max}=0.741$, 0.950). The structure was solved by the Patterson methods and difference Fourier synthesis. On the basis of successful solution and refinement of the structures, the space group was determined to be *P*-1 (No. 2). The In and Ge atoms were initially located and the O, C, N, and B atoms were found in the difference Fourier maps. Bond–valence calculation indicated that all O atoms other than O(3) and O(8) were saturated. The two atoms, O(3) and O(8), had valence sums of 0.99 and 1.13, respectively, and then were assigned to hydroxo oxygen groups. The H atoms bonded to C atoms in the 1,2-diaminopropane molecule were positioned geometrically and refined using a riding model with fixed isotropic thermal parameters. The hydrogen atoms associated with nitrogen atoms, oxygen atoms, and water molecules could be located in difference Fourier maps except that those with Ow(2) could not be located. The presence of water molecules in the structure is also supported by the thermogravimetric analysis which displays weight loss of 6.83% between 40 and 200 °C (calcd. 7.07%). The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters of H atoms converged at $R_1=0.0362$, $wR_2=0.1083$, and $S=1.06$ for **1.** All the calculations were performed using the SHELXTL Version 5.1 software package. The crystal data and selected bond lengths are given in Tables 1 and 2, respectively. Crystallographic Data Center as supplementary publication no. CCDC-931681. The data can be obtained free of charge via the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Table 1
Crystallographic data for $InBGe_2O_6(OH)_2(1,2\text{-DAP})\cdot 2H_2O$ (**1**).

Crystal size (mm)	0.10 × 0.10 × 0.07
Crystal system	triclinic
Space group	*P*-1 (No. 2)
a (Å)	6.9459(9)
b (Å)	8.836(1)
c (Å)	11.023(2)
α (°)	85.958(9)
β (°)	87.853(9)
γ (°)	79.441(8)
V ($Å^3$)	663.2(2)
Z	2
fw	510.99
λ(Mo *K*α), Å	0.71073
ρ_{calc} (g cm^{-3})	2.559
μ(Mo *K*α) (mm^{-1})	6.27
$2\theta_{\max}$ (°)	55.48
Unique data ($I>2\sigma(I)$)	2556
R_1[a]	0.0362
wR_2[b]	0.1083
GOF	1.06

$P=[\mathrm{Max}(F_o,0)+2(F_c)^2]/3$, where $a=0.063$ and $b=1.51$.
The highest peak and the deepest hole locate at 1.06 Å from H(2A) and 61 Å from Ow(2).

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2=\Sigma\{[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_{o2})^2]\}^{1/2}$, $w=1/[\sigma^2(F_o{}^2)+(aP)^2+bP]$.

Table 2
Bond lengths (Å) for $InBGe_2O_6(OH)_2(1,2\text{-DAP})\cdot 2H_2O$ (**1**).

In(1)–O(1)[a]	2.088(3)	In(1)–O(6)[b]	2.156(3)
In(1)–O(6)	2.177(3)	In(1)–O(8)	2.212(2)
In(1)–N(1)	2.251(4)	In(1)–N(2)	2.231(3)
Ge(1)–O(1)	1.722(3)	Ge(1)–O(2)	1.757(3)
Ge(1)–O(3)	1.752(3)	Ge(1)–O(4)	1.768(3)
Ge(2)–O(4)	1.753(3)	Ge(2)–O(5)	1.743(3)
Ge(2)–O(6)	1.742(3)	Ge(2)–O(7)	1.740(3)
B(1)–O(2)[c]	1.480(5)	B(1)–O(5)[d]	1.468(5)
B(1)–O(7)	1.456(5)	B(1)–O(8)[d]	1.505(5)

Symmetry transformations used to generate equivalent atoms:

[a] $x-1, y, z$.

[b] $-x-1, -y, -z+3$.

[c] $-x, -y+1, -z+3$.

[d] $-x-1, -y+1, -z+3$.

3. Results and discussion

3.1. Description of the structures

The structure crystallizes in the centrosymmetric space group *P*-1 (No. 2), and all atoms are in general positions. The structure of **1** is constructed of one InO_4N_2 octahedron, one GeO_4 tetrahedron, one $GeO_3(OH)$ tetrahedron, one $BO_3(OH)$ tetrahedron and one neutral 1,2-DAP molecule. The In atom is bonded to two N atoms from a 1,2-DAP chelate and O atoms from three germanates and one borate to form a distorted InO_4N_2 octahedron. Each indium polyhedron shares its O···O edge to generate an $In_2O_6N_4$ octahedral dimer incorporating two chelating amine ligands in opposite positions (Fig. 1a). Bond–valence calculations indicate that all of the O atoms, except O(3) and O(8), are saturated. These two atoms, O(3) and O(8), have valence sums of 0.99 and 1.13, respectively, and thus are assigned to hydroxo oxygen groups. All of the Ge and B atoms are tetrahedrally coordinated, either by oxygen atoms or by hydroxo oxygen atoms. The Ge–O and B–O bond lengths are 1.722–1.768 and 1.456–1.505 Å, respectively. The two Ge tetrahedral are joined through corner-sharing oxygen to form a $Ge_2O_6(OH)$ double tetrahedron, which are further connected by $BO_3(OH)$ groups to form double chains (Fig. 1b). This kind of double chains with four- and six-membered rings have been observed in **1** and in okenite ($Ca_{10}Si_{18}O_{46}\cdot 18H_2O$), but different from their topologies and from the distribution of tetrahedra