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A Novel Boron Oxide Organic Open-Framework Compound: $B_6O_9(en)_2@(H_2en)Cl_2$

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A new boron oxide organic open-framework compound with $(H_2en)Cl_2$ as a template was synthesized solvothermally and characterized by various techniques such as elemental analysis, IR spectroscopy, X-ray diffraction, thermogravimetric analysis, and luminescence. The framework is built up from neutral $[B_6O_9]$ layers linked by ethylenediamine molecules through coordinative B–N bonds.

Introduction

Borate materials have received much attention in the last decades, not only owing to their intriguing variety of architectures, but also as a result of their numerous applications in mineralogy,[1] nonlinear optics,[2] and photoluminescence.[3] In recent years, the successful introduction of various organic moieties into the borate system has opened a new way to synthesize borate materials, and an increasing number of borate-containing organic molecules have been reported. However, most of these borates consist of isolated,[4,5] layered,[6] or open-frameworked[7] boron polyanions formed by organic templates, and borates with inorganic–organic hybrid frameworks containing coordinative B–N bonds are rare.[5,7,8]

From the viewpoint of structural chemistry, boron atoms may bond to oxygen either in three-coordinate BO_3 or four-coordinate BO_4 groups, and two kinds of units may polymerize by sharing oxygen atoms to form isolated rings/cages or infinite chains, sheets, and frameworks. Besides, the three-coordinate BO_3 groups also can be coordinated by nitrogen atoms because of the electron-deficient character of boron. Therefore, the prediction or design of borates is still an ongoing challenge. In our experiment, we anticipated that a new borate would be synthesized by the choice of 1,4-diazabicyclo[2.2.2]octane as a template under solvothermal conditions. Unexpectedly, a novel open-framework compound, $B_6O_9(en)_2@(H_2en)Cl_2$ (**1**) (en = ethylenediamine), was obtained. Herein, the synthesis and structural characterization of **1** are presented.

Results and Discussion

Single-crystal X-ray diffraction analysis revealed that the structure of **1** is built up from extended neutral $[B_6O_9]$ layers linked by ethylenediamine molecules through coordinative B–N bonds, giving rise to a hybrid open framework with 24-membered channels along the *c* direction. Channels are also formed by the linkers of ethylenediamine in the *a* and *b* axis, as shown in Figure 1. The channels are occupied by $(H_2en)Cl_2$, which is a template and is essential to the formation of the open framework, as it prevents the interpenetration of neutral nets. Notably, the borate with an inclusion is rare,[9] and compound **1** is the only one with an inclusion in non-metal boron oxide organic compounds.

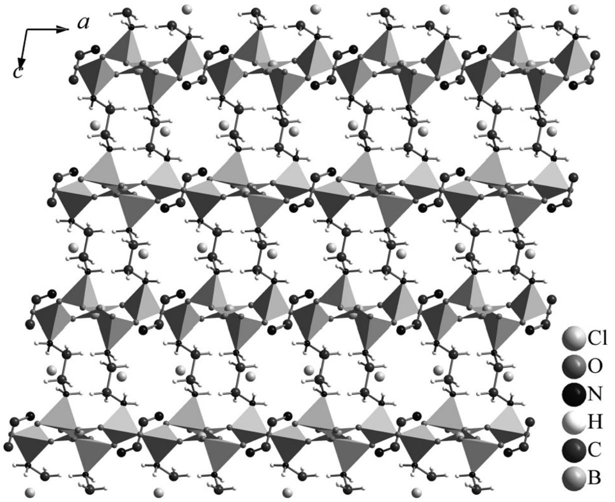

Figure 1. The crystal structure of **1**, which is built up from neutral $[B_6O_9]$ layers linked by ethylenediamine molecules through tetrahedral boron atoms. The templates, $(H_2en)Cl_2$, reside in the channels. Hydrogen atoms of $(H_2en)Cl_2$ are omitted for clarity.

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The fundamental building block (FBB)[10] of neutral 2D [B_6O_9] layers, which can be described as 4□2△<△2□><△2□>,[10] consists of two six-membered rings each comprising one triangular (△) BO_3 and two tetrahedral (□) BO_3N groups. The neighboring FBBs are linked by sharing oxygen atoms to form extended layers, as shown in Figure 2. To our awareness, the FBB of the 2D layers in **1** is a new type in 2D borate compounds. The average B–O distances around three- and four-coordinate boron atoms are 1.364 and 1.443 Å, respectively. These distances are within the typical range for borate compounds.[4–6] The average B–N distance in BO_3N tetrahedra is 1.661 Å, which is quite normal for a coordinative B–N bond.[11]

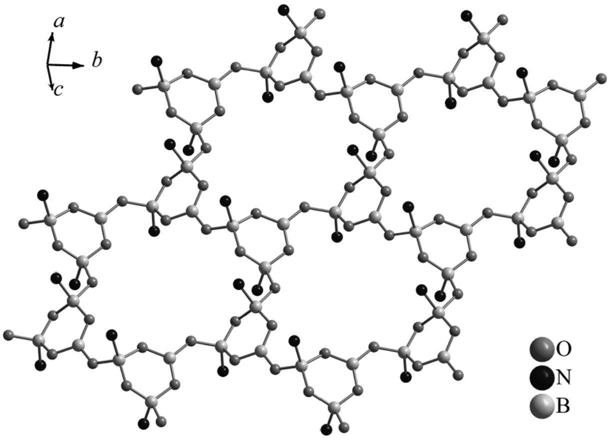

Figure 2. The neutral [B_6O_9] layer, in which the B_6O_9 FBB contains two six-membered rings, each comprising one triangular BO_3 and two tetrahedral BO_3N groups.

It is worthwhile to compare the structure of **1** with previously reported B_6O_9(en) (**2**), which also includes ethylenediamine molecules to link BO_3 groups.[7] There are distinctive differences between the structures of **1** and **2**: Compound **1** is a 3D open framework with (H_2en)Cl_2 molecule-filled channels, whereas **2** is a 3D interpenetrating framework. They also differ in the B_6O_9 FBB of neutral layers, the FBB is 4□2△<△2□><△2□> in **1**, in contrast to 2□4△<2△□><2△□> in **2**. It was reported that six-membered rings having one triangular and two tetrahedral boron atoms (△2□) are more energetically stable than other configurations.[12]

In order to examine the stability of the framework, thermogravimetric analysis (TGA) of **1** was carried out under a flow of nitrogen (40 mL min^{-1}) from 30 to 580 °C with a heating rate of 10 °C min^{-1}. The TGA curve shows that there is no significant weight loss up to about 270 °C, and then a two-step weight loss is observed. The initial mass loss between 270 and 420 °C can be attributed to the liberation of the (H_2en)Cl_2 inclusions and half of the en molecules in the framework (weight loss found 38.06%; calcd. 41.68%), which results in collapse of the framework. It showed that the framework of **1** was not stable to the thermal removal of the template. The later loss, occurring between 420 and 580 °C, corresponds to the release of the remaining en molecules in the framework (found 10.74%; calcd. 12.96%). Powder X-ray diffraction measurements indicated that the final residue was amorphous.

The luminescence properties of **1** in the solid state were investigated at room temperature. As shown in Figure 3, compound **1** can be excited by light with a wavelength ranging from 315 to 415 nm, and a blue photoluminescence occurs with an emission maximum at 457 nm upon excitation at 367 nm. The template (H_2en)Cl_2 shows no luminescence properties; therefore, the luminescence properties should originate from the boron oxide organic framework rather than the isolated templates. These emission bands are similar to those of (H_2en)$_2$(Hen)$_2B_{16}O_{27}$ (**3**).[7] The difference in maximum emission positions between **1** and **3** may be attributed to the different coordination modes around the B atoms.

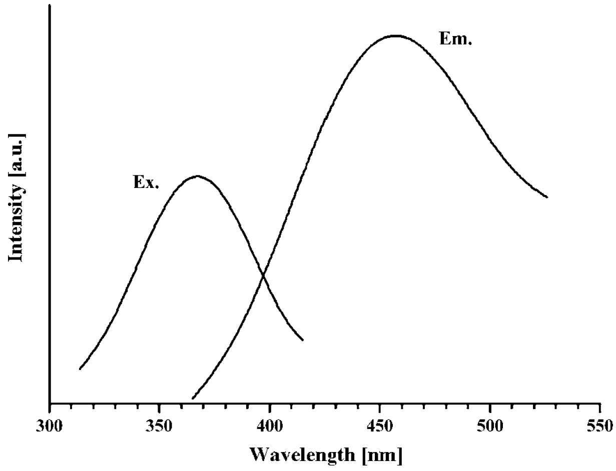

Figure 3. Excitation and emission spectra of **1**: compound **1** exhibits a blue photoluminescence with an emission maximum at 457 nm upon excitation at 367 nm.

Conclusions

In conclusion, the successful synthesis of a boron oxide organic open-framework compound offers a new possible avenue for the construction of diverse new open-framework borate materials with desired channels and functions through the choice of various organic diamine linkers. In principle, it is also possible to create open-framework borate materials with ion-exchange properties by choosing certain diols as the linkers. The related research is in progress in our laboratory.

Experimental Section

Synthesis: Compound **1** was prepared by the solvothermal reaction of H_3BO_3 (0.018 g), 1,4-diazabicyclo[2.2.2]octane (0.066 g), 38% HCl (0.03 g), en (0.105 g) in pyridine (0.675 g). The mixture was sealed in a Pyrex glass tube with ca. 10% filling at room temperature, placed into a stainless-steel autoclave, and then heated at 443 K for 6 d. After being cooled naturally to ambient temperature, the products were washed with ethanol, and the colorless block crystals were obtained in 53.5% yield (12.0 mg) based on boron. These colorless crystals are dissoluble in water, but insoluble in common organic solvents (methanol, ethanol, acetonitrile, benzene, ethyl ether, tetrachloromethane). The pure phases of **1** were confirmed by comparing powder X-ray diffraction patterns of the bulk sample with the calculated pattern from the single-crystal structure. $C_6H_{26}B_6Cl_2N_6O_9$ (462.09): calcd. C 15.59, H 5.67, N 18.19; found C 15.65, H 5.64, N 18.21. IR (KBr pellet): $\tilde{\nu}$ = 3425 [m, ν(N–H), ν(O–H)], 3164 [s, $\nu(NH_3^+)$], 3097 [s, ν(C–H)], 1635 [m, δ(N–H)], 1601 [m, δ(N–H)], 1454 [w, δ(C–H)], 1416 [w, $\nu(BO_3)$], 1307 [m, $\nu(BO_3)$], 1169 [vw, ν(C–N)], 1050 [vs, $\nu(BO_4)$], 998 [m, $\nu(BO_4)$] cm^{-1}.

Physical Measurements: Powder X-ray diffraction (XRD) data of **1** were reported by using an XRD-6000 X-ray diffractometer with Cu-K_α radiation. The elemental analysis of **1** was performed with an Elementar Vario EL III elemental analyzer. IR spectra of **1** were obtained with a Nicolet360 FTIR spectrophotometer in KBr matrix in the range 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) of **1** was carried out by Metter Toledo Star under a flow of nitrogen (40 $mL\,min^{-1}$) from 30 to 580 °C at a heating rate of 10 $°C\,min^{-1}$. The fluorescence spectra of **1** in the solid state at room temperature were collected by using a Hitachif-4500 fluorescence spectrophotometer.

Crystal Data for 1: $B_6O_9(en)_2@(H_2en)Cl_2$, Fw = 462.09, monoclinic, $C2/c$, a = 15.1032(16) Å, b = 8.7460(10) Å, c = 14.5672(15) Å, β = 100.081(6)°, V = 1894.5(4) $Å^3$, Z = 4, $D_{calcd.}$ = 1.620 $g\,cm^{-3}$, R = 0.0331, R_w = 0.0899, all 1648 reflections were used. Data collection was performed with a Bruker Smart APEX II diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. CCDC-715127 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): XRD patterns, IR spectrum, and a TGA plot for compound **1**.

Acknowledgments

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