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Cotemplating Synthesis of a Rare Borate $Ni(en)_3 \cdot Hen \cdot [B_9O_{13}(OH)_4] \cdot H_2O$ with a Chiral Polyanonic Chain Constructed from Two Different Clusters

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S *Supporting Information*

ABSTRACT: $Ni(en)_3 \cdot Hen \cdot [B_9O_{13}(OH)_4] \cdot H_2O$ was prepared under the cotemplating effect of $[Ni(en)_3]^{2+}$ and Hen^+. It was the first example of a cotemplated borate with an unusual chiral polyanionic chain, which was constructed from $[B_5O_8(OH)_2]$ and $[B_4O_7(OH)_2]$ clusters.

Great attention has been paid to the hydro- or solvothermal preparation of templated borates, owing to their intriguing variety of architectures and potential applications, such as mineralogy, nonlinear optics, and photoluminescence.[1] Boron is of particular interest because it shows flexible coordination numbers, namely, $[BO_3]$ triangle and $[BO_4]$ tetrahedron, which have the ability to form a great variety of boron−oxygen (BO) polyanions,[2−5] including $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_5^{2-}$, $B_8O_{10}(OH)_6^{2-}$, and so on. It is believed that the synthesis of these polyanions are mainly dependent upon the boron concentration, pH, and temperature.[2] So far, a combination of polyanions and organic cations has resulted in the discovery of a great number of templated borates. Although significant progress has been made in this domain, relatively few borates have been found to have high-dimensional polyanionic frameworks such as chains,[4] sheets,[5] and networks.[6] A synthetic route to an extended borate structure discovery is integration of a heteroatom into a borate framework. Studies performed on templated borate constructed from BO clusters and metal ions have been confirmed in the synthesis of a series of borates with extended structure. As exemplified, the incorporation of metal ions (e.g., Al^{3+},[7] Ga^{3+},[8] Ge^{4+},[9] Zn^{2+},[10] etc.) has led to the formation of a series of three-dimensional borates.

Hydro- or solvothermal synthetic crystals of templated compounds with a variety of structures are mainly based on the use of organic amine as the template. For further studies of the directing effect of templates, some efforts are being dedicated to preparing new materials by means of employing two types of organic amines, which can help to cooperatively direct the formation of inorganic host frameworks with a rich variety of structures.[11] The role of two types of organic amines has usually been described as a "cotemplating effect".[11g] The cotemplating synthesis has been proven useful for the preparation of a large number of microporous silicates and phosphates.[11] To enrich the connection mode of BO clusters and metal ions, some groups attempted to prepare metal borates under the direct effect of a cotemplate, but little progress has been made.[7f] Up to now, no BO polyanionic framework synthesized by a cotemplated method has been documented, to the best of our knowledge. As a continuation of systematic research on a templated borate, we are interested in applying an organic amine and a metal complex (MC) as a cotemplate to the borate system and further researching their role in determining the host framework structure. The exploration of MCs as a new cotemplate composition is not a random choice but a deliberate selection. The compounds directed by MCs have attracted considerable attention[12] because the MCs have various charges, hydrogen-bonding sites, unique spatial configurations, and different flexibilities, which not only generate a variety of unusual frameworks but also can integrate the electronic, optical, and magnetic properties of MCs with the host inorganic framework.

Herein, we demonstrate a typical example of cotemplating synthesis of a new borate $Ni(en)_3 \cdot Hen \cdot [B_9O_{13}(OH)_4] \cdot H_2O$ (denoted as **1**, where en = ethylenediamine). **1** is the first example of a cotemplated borate in which a chiral polyanionic chain was observed. Meanwhile, **1** crystallizes in monoclinic space group *Pn*, which belongs to one of 10 polar groups (C_1, C_2, C_s, C_{2v}, C_3, C_{3v}, C_4, C_{4v}, C_6, C_{6v}); such space groups are indispensable to ferroelectric properties. Its ferroelectric, para-electric as well as magnetic property have been investigated systematically. **1** was prepared by mixture of H_3BO_3, $NiCl_2 \cdot 6H_2O$, *N*,*N*-dimethylformamide (DMF), en, and 3-nitrophenylboronic acid with a mole ratio of 7.7:0.5:25.9:44.9:0.8 at 180 °C for 7 days in a 28 mL Teflon-lined stainless steel autoclave. Single-crystal X-ray analysis reveals that the title compound can be formularized as $C_8H_{30}B_9N_8NiO_{17}$. All non-H atoms were refined anisotropically. The asymmetrical unit of **1** reveals 1 Ni atom, 9 B atoms, 18 O atoms, 8 C atoms, and 8 N atoms (Figure 1a). In detail, Ni is coordinated by six N atoms from the three amine molecules to form a $[Ni(en)_3]^{2+}$ cation, a protonated cation Hen^+, and one water molecule. B is coordinated by O atoms and −OH groups to form four $BO_2(OH)$ (B1, B3, B6, and B8) and two BO_3 (B5 and B9) triangles, as well as three BO_4 tetrahedra (B2, B4, and B7). The B−O bond lengths vary from 1.329 to 1.400 Å for the BO_3 triangles and from 1.444 to 1.512 Å for the BO_4 tetrahedra. The O−B−O bond angles are distributed in the range of 114.3(4)−123.2(4)° for the triangles and 104.6(3)−115.2(4)° for the tetrahedra.

The connectivity of the triangular BO_3 and tetrahedral BO_4 units gives rise to two different clusters, $[B_5O_8(OH)_2]$ and $[B_4O_7(OH)_2]$. The strictly alternating $[B_5O_8(OH)_2]$ and

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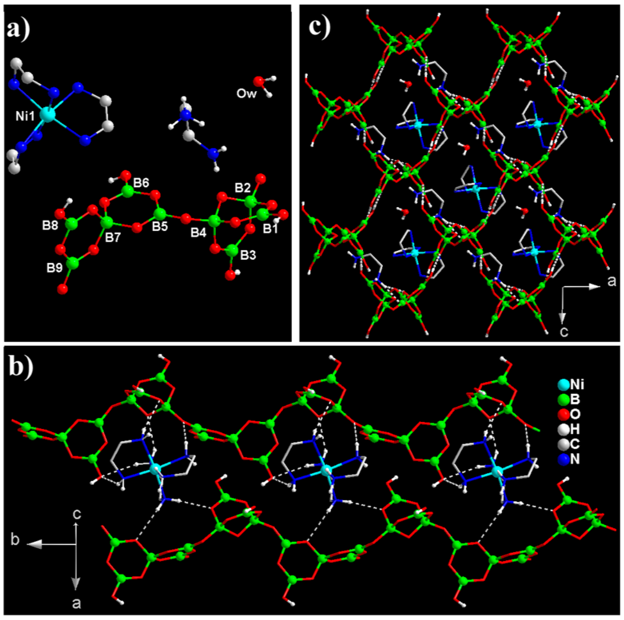

Figure 1. (a) View of the coordination environment of B and Ni atoms in an asymmetric unit. (b) View of a $[B_9O_{13}(OH)_4]_n$ chain constructed from $[B_5O_8(OH)_2]$ and $[B_4O_7(OH)_2]$ clusters and view of H-Bs between MCs and an inorganic skeleton to show host–guest symmetry. (c) View of MCs, organic cations, and waters located in the 14-membered ring channels.

$[B_4O_7(OH)_2]$ clusters form an infinite polyanionic chain, formularized as $[B_9O_{13}(OH)_4]_n$, as shown in Figure 1b. $[B_5O_8(OH)_2]$ consists of four trigonal groups [two B(6,8)-$O_2(OH)$ and B (5,9)O_3 units] and one tetrahedral group [B(7)O_4], in which the trigonal groups are linked together by one common BO_4 tetrahedron. $[B_4O_7(OH)_2]$ consists of two $\{B_3O_3\}^{3-}$ membered rings, in which two trigonal groups B(1,3)$O_2(OH)$ and two tetrahedral B(2,4)O_4 units are linked by common O atoms. $[B_5O_8(OH)_2]$ and $[B_4O_7(OH)_2]$ clusters have been found in many borates. However, the coexistence of $[B_5O_8(OH)_2]$ and $[B_4O_7(OH)_2]$ in a borate crystal cell is a rare find because synthesis of these two types of BO clusters is mainly dependent on different pH values, boron concentrations, and temperatures. With the exception of inorganic borates,[2b] only one organoamine templated borate with a one-dimensional structure was reported, in which $[B_5O_7(OH)_3]$ clusters did not participate in building the one-dimensional framework but just grafted onto the $[B_3O_6(OH)]$ chain. Therefore, the $[B_9O_{13}(OH)_4]_n$ chain constructed from $[B_5O_8(OH)_2]$ and-$[B_4O_7(OH)_2]$ clusters is an unexpected structural motif. Another interesting aspect for **1** is that $[B_9O_{13}(OH)_4]$ is a chiral chain. The chirality of this chain was induced by guest complex cations through hydrogen bonds (H-Bs) according to host–guest symmetry.[9b,13] It has been shown that the symmetry of guest $[Ni(en)_3]^{2+}$ cations is important for the self-assembly process of **1**, wherein the host framework was imprinted by a chiral $[Ni(en)_3]^{2+}$ guest through H-Bs, as shown in Figure 1b,c. The symmetry of host chains is determined by ordered chiral $[Ni(en)_3]^{2+}$ guest cations. The chain coincides with the symmetry element of each individual $[Ni(en)_3]^{2+}$ guest. In a word, chiral $Ni(en)_3^{2+}$ leads to the chirality of an inorganic chain. In detail, $[Ni(en)_3]^{2+}$ has two kinds of Δ and Λ configurations, but only Δ-$[Ni(en)_3]^{2+}$ is observed in the structure of **1**. It is believed that the cooperative direct effect of $Ni(en)_3^{2+}$ and Hen^+ plays a crucial role in the formation of such unusual structures.

The whole framework of **1** was stabilized by extensive H-Bs involving a $[B_9O_{13}(OH)_4]$ chain, a templated cation, and water, in which the chains are linked together by O–H···O (H···O distance: 1.86–2.05 Å), forming a network containing 14-membered ring channels along the *b* axis, as shown in Figure 1c. $[Ni(en)_3]^{2+}$ and Hen^+ cations reside in the channels and interact with the chains through N–H···O H-Bs (H···O distance: 1.90–2.57 Å). The multipoint H-B interactions play an important role in the stability of a low-dimensional structure.

For ferroelectric measurements, the samples were prepared in the form of 1.79-mm-thick plates with silver paste deposited on the surfaces at room temperature. Experimental results show that the compound displays ferroelectric behavior at room temperature. Figure 2 shows the electrical hysteresis loop observed when an electric field between −28 and +28 kV was applied to the sample. Spontaneous polarization (P_s of about 0.052 $\mu c/cm^2$) occurred during the measurement conditions with remnant polarization (P_r of about 0.030 $\mu c/cm^2$) and a coercive field (E_c) of about 28 kV/cm. It exhibits a wide E_c value of ca. 4–28 kV/cm in new ferroelectric crystallites. In a comparison of KH_2PO_4-type ferroelectrics,[14] P_s of **1** is very close, probably because the mechanism leading to the ferroelectricity in the compound is similar to that of the examples of KH_2PO_4-type ferroelectrics, where spontaneous polarization occurs perpendicularly to the H-Bs. Proton transfer or disorder can change the polarization of the crystal, which plays a key role in the mechanism of ferroelectric phase transition in the compound. The dielectric properties of **1** have been investigated, and plots of the dielectric constant (ε′) versus temperature and the dielectric loss [tan(δ)] versus

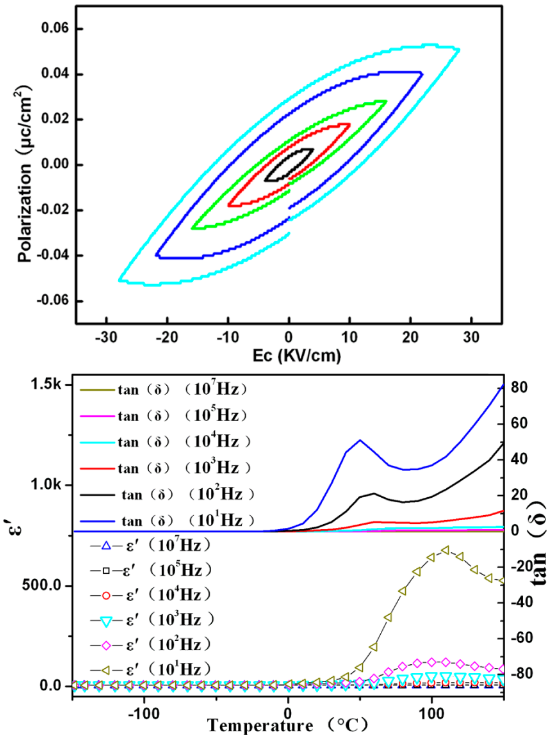

Figure 2. (Top) Electric hysteresis loop of a plate obtained from a powered sample of the title compond at room temperature (50 Hz). (Bottom) Temperature dependence of the dielectric constant and dielectric loss at various frequencies (10^1–10^7 Hz).

temperature at different frequencies as well as the frequency dependence of ε' and tan(δ) at different temperatures are displayed in Figures 2 and S1 in the Supporting Information (SI). These figures show that, first, **1** has constant ε' (av. 4.8) and tan(δ) (av. 3×10^{-3}) and, second, constant and dielectric losses rapidly increase above 0 °C; a peak maximum appears in the plots of ε' and tan(δ) at 110 and 50 °C, respectively, when the frequency is 10 Hz; third, no obvious peaks are observed below 40 °C, indicating that no ferroelectric or paraelectric−ferroelectric phase transition happens under lower temperature; the results are consistent with the differential scanning calorimetry (DSC) curves in Figure S2 in the SI, showing that **1** is thermally stable from −150 to +40 °C.

The variable-temperature susceptibility measurements of **1** were performed in the range of 1.8−300 K at a magnetic field of 1 kOe. As shown in Figure S3 in the SI, from 300 K to around 65 K the value of $\chi_M T$ is approximately constant, revealing a paramagnetic behavior. The obtained Curie constant for samples is ca. 1.10 emu·K/mol. The corresponding effective moment is $\mu_{eff} = 2.966\ \mu_B$. This agrees well with the expected theoretical spin-only value for a noninteracting $S = 1$ magnetic ion of Ni^{2+}.[15] The decrease in $\chi_M T$ upon decreasing temperature from 60 to 2 K can be attributed to a zero-field splitting of the Ni^{2+} ion with a d^8 configuration in axially distorted octahedral surroundings as follows from the structural determination. Fitting the global high-temperature susceptibility to the Curie−Weiss law results in the values of $C = 1.15$ emu·K/mol and $\theta = -0.52$ K.

In summary, we have successfully synthesized a new cotemplated borate directed by $Ni(en)_3^{2+}$ and Hen^+ cations. We have shown that a combination of different types of BO clusters provides more possibilities of designing novel frameworks such as chiral chains. The physical properties of **1** were performed and discussed, indicating that it may be an attractive material for applications in the field of electronic devices. We hope that this work will stimulate more interest in cotemplated borates. Further investigation on this work is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file (CCDC 1012579), synthesis, element analysis, measurement of DSC-TG, PXRD patterns, magnetic data, IR spectra, and frequency dependence of dielectric constant ε' and dielectric loss tan(δ). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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