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Synthesis, crystal structure and visible light emission of a new inorganic–organic hybrid pentaborate, $[C_6H_{14}N][B_5O_6(OH)_4]$

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HIGHLIGHTS

- A new organically templated pentaborate $[C_6H_{14}N][B_5O_6(OH)_4]$ has been synthesised.
- Tunable blue and near-white emissions are achieved by simple heating treatment.
- Such organic-inorganic hybrid borates are potential for display and lighting applications.

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ABSTRACT

A new organic–inorganic hybrid pentaborate $[C_6H_{14}N][B_5O_6(OH)_4]$ (**1**) has been synthesised hydrothermally in aqueous solution and characterised by single-crystal X-ray diffraction, FT-IR, DTA-TG and photoluminescence spectroscopy. It crystallizes in the monoclinic system, space group $P2_1/c$, with the lattice constants of $a = 9.463\ (2)$ Å, $b = 14.005\ (3)$ Å, $c = 10.642\ (2)$ Å, and $\beta = 93.82(3)°$. The structure consists of isolated $[B_5O_6(OH)_4]^-$ groups interlinked by protonated cyclohexylamine via hydrogen bonding. Blue photoluminescence of **1** is observed upon UV excitation, which can be further enhanced and modified to near-white emission by thermal treatment. The maximum emissions and peak shapes of **1**–250 °C are also tunable with various excitation wavelengths in the region of 350–470 nm. This compound provides a novel example of organically templated borate materials potential for display and lighting applications.

1. Introduction

The large family of borate materials have provided an expansive area of research in the last decades owing to their rich structural chemistry [1–3] and important applications as nonlinear optical (NLO) crystals [4–7], luminescent host materials [8–11], lithium battery electrodes [12–14], and porous open-frameworks for catalysis and separation [15,16]. The structural diversity of borates benefits from the flexibility of boron atoms to adopt either trigonal or tetrahedral coordination configuration to generate the basal BO_3, BO_4 and derived groups formed by their linkages, which gives opportunity for specific structure design by crystal engineering method. Particularly, the recent experimental strategies involving organic-amines in hydrothermal syntheses have broken an effectual path to achieve a series of new organically templated borate materials [17–24]. The resulting hybrid materials exhibit various structure features consisting of either isolated boron–oxygen polyanions via hydrogen bonding or covalently connected 3-dimensional (3D) open-frameworks.

Recently, Wang et al. [25] reported the synthesis and luminescence properties of $(H_2en)_2(Hen)_2B_{16}O_{27}$ (en = ethylenediamine), the first example of a borate-based inorganic–organic hybrid open framework exhibiting efficient white-light-emitting. And it was followed by several other similar examples such as $B_6O_9(en)_2@(H_2en)Cl_2$, $[C_6N_4H_{20}]_{0.5}[B_5O_6(OH)_4]$ and $[C_6H_{16}N][B_5O_6(OH)_4]$ [26–28]. The photoluminescence in these hybrid materials can be modified from blue to white by means of a simple heat-treatment process, which makes them as potential candidates for display and lighting applications. However, the emission mechanism of such non-metal materials is not very clear now, for that all of the authors have attributed the light emitting to the oxygen defects, the same as that in B_2O_3 glass. But one should be aware that the fabrication condition of those crystalline compounds (mild hydrothermal

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Table 1
Details of data collection and structure refinement results of **1**.

Formula	$C_6NB_5O_{10}H_{18}$
Temperature	293 K
Wavelength	0.71073 Å
Symmetry	Monoclinic, $P2_1/c$
Cell parameters	$a = 9.4628(2)$ Å, $b = 14.005(3)$ Å, $c = 10.642(2)$ Å, $\beta = 93.82(3)°$, $V = 1407.2(5)$ Å^3
Z	4
$D_{calc.}$ (g cm^{-3})	1.502
μ (mm^{-1})	0.130
Scan range (°)	2.16–33.68
Independent reflns	5601
Reflns with $I > 2\sigma(I)$	3710
GOF on F^2	1.057
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.056$, $wR2 = 0.149$
R indices (all data)	$R1 = 0.081$, $wR2 = 0.166$
Residual electron density (e Å^{-3})	0.518/−0.347

conditions) differs much from that of the glass formation. Moreover, in our recent studies towards organic-amine incorporated boron–oxygen molecule systems, it's found that even the polymers with similar B/O/N compositions can emit intense visible luminescence. To explore the actual fact, more samples and characterisations are needed. Here we report the synthesis and crystal structure of cyclohexane templated pentaborate $[C_6H_{14}N][B_5O_6(OH)_4]$, a new member in the organic-amine hybrid borate family with interesting visible light emitting properties. This compound exhibits tunable blue and near-white emissions by annealing at different temperatures and changed excitation wavelengths, which provides an additional example to explore the emitting mechanism in such systems.

2. Experimental

All reagents were of analytical grade and were used as obtained by commercial sources without further purification. The title compound $[C_6H_{14}N][B_5O_6(OH)_4]$ (**1**) was synthesised hydrothermally from a mixture of H_3BO_3 and cyclohexylamine ($C_6H_{13}N$) with B/N molar ratio of 5/1 in aqueous solution. Typically, 1.237 g H_3BO_3, 0.397 g $C_6H_{13}N$ and 15 ml distilled H_2O were combined under vigorous stirring for 20 min at room temperature. The resulting viscous mixture was transferred to a Teflon-lined autoclave and heated at 170 °C for 5 days and then cooled to room temperature. Colourless crystals were collected, washed with alcohol several times and dried at 80 °C over night. For the heat treatment, 0.5 g powder sample of **1** was placed in an alumina crucible, annealed at 200, 250, 300 °C for 5 h, respectively. And the resulting products under different temperatures are denoted as follows: **1**-RT, **1**–200 °C, **1**–250 °C, **1**–300 °C.

Suitable single crystal of **1** ($0.14 \times 0.12 \times 0.10$ mm^3) was selected for single-crystal X-ray diffraction measurement. Intensity data were collected on a Rigaku Mercury diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by using the ω-scan mode at room temperature. The data absorption corrections were applied based on CrystalClear program [29] and the structure was solved and refined by using SHELXS-97 and SHELXL-97 programs [30,31], respectively. The crystallographic parameters for **1** are summarised in Table 1. FT-IR spectra were recorded on a NICOLET iN10MX spectrum instrument as KBr pellets in the range of 4000–400 cm^{-1}. Differential thermoanalyses and thermogravimetry (DTA–TG) analyses were performed in an air atmosphere with a heating rate of 10 °C/min from 50 to 900 °C, using a NETZSCH STA449C instrument. All of the PL spectra were recorded on a FLS920 spectrophotometer (Edinburgh Instrument Ltd.) at room temperature.

3. Results and discussion

The title compound **1** crystallizes in the monoclinic system, space group $P2_1/c$, with the lattice constants of $a = 9.463$ (2) Å, $b = 14.005$ (3) Å, $c = 10.642$ (2) Å, $\beta = 93.82(3)°$, and the detailed data are listed in Table S1. The crystal structure is composed of isolated $[B_5O_6(OH)_4]^-$ anions and protonated cyclohexane to form a 3-dimensional framework via hydrogen bonding (Fig. 1). The pentaborate anion $[B_5O_6(OH)_4]^-$ contains four BO_3 triangles and one bridging BO_4 tetrahedron linked to each other, and the four terminal oxygen atoms are protonated, which is similar to that in many borate compounds such as the "santite" $KB_5O_8{\cdot}4H_2O$. The average B–O bond length for triangularly and tetrahedrally coordinated boron atoms are 1.355 Å and 1.457 Å, respectively. The O–B–O bond angles vary from 107.5° to 111.0° in BO_3 triangles and from 115.1° to 123.5° in BO_4 tetrahedra, all of which are quite regular and in accordance with expectation. For more bond length and bond angle information, see Appendices, Table S2. Moreover, it is worth mentioning that the O–H···H hydrogen bonds in the structure exist not only between the polyborate anions and protonated organic-amine cations, but also between the neighbouring [B_5O_6

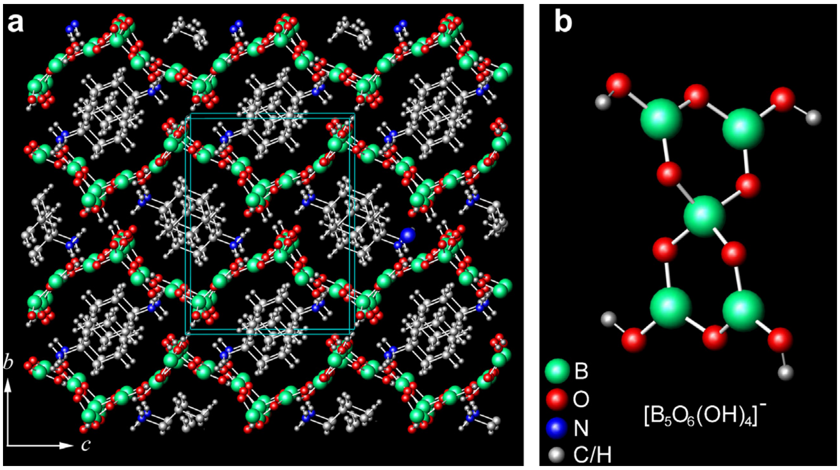

Fig. 1. (a) The crystal structure of **1** viewed along the a direction; (b) The isolated $[B_5O_6(OH)_4]^-$ groups as the basic building units in the hydrogen-bonding connected structure of **1**.