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Short communication

An inorganic-organic hybrid solid with $B_5O_7(OH)_3$ clusters bridged and decorated by zinc–amine complexes

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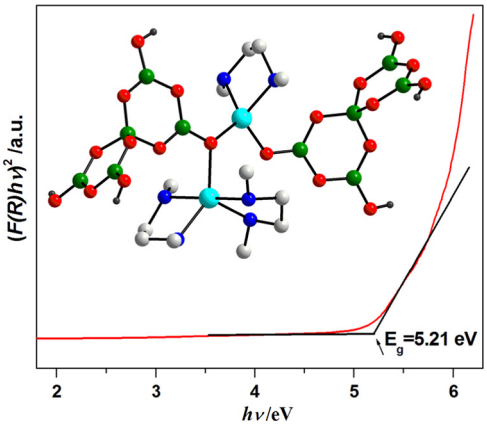
GRAPHICAL ABSTRACT

An inorganic-organic hybrid zinc borate was prepared under solvothermal conditions. It has a dimeric structure containing two oxo boron clusters and two different zinc–amine complexes. This compound is a direct-gap material with a band gap of 5.21 eV.



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ABSTRACT

A new inorganic-organic hybrid solid, namely, $Zn_2(dmen)_3B_{10}O_{14}(OH)_6$ (dmen = *N*, *N*′-dimethylethylenediamine) was prepared under solvothermal conditions. This compound has a molecular structure with $B_5O_7(OH)_3$ clusters bridged and decorated by zinc–amine complexes. It is a direct-gap material with a band gap of 5.21 eV. The band structure and density of states of the compound were also calculated based on density functional theory.

Open-framework metal borates emerge as an important class of solid state materials because of their rich structures and appealing properties such as luminescence, catalysis, and second harmonic generation response [1–4]. Different from zeolite molecular sieves built from TO_4 (T = Si, Al) tetrahedra, metal borates often contain BO_3 triangles and BO_4 tetrahedra as their structural building units [5–9]. Notable compounds include the thorium borate NDTB-1 with a supertetrahedral cationic framework, the inorganic-organic hybrid solid $[Zn(dap)_2][AlB_5O_{10}]$ possessing independent aluminoborate framework and zinc-amine coordination network, and the cobalt borate $Na_2Co_2B_{12}O_{21}$ containing exchangeable Na^+ cations [10–12]. It is worth noting that BO_3 triangles and BO_4 tetrahedra have a great tendency to aggregate and form different oxo boron clusters, such as $B_3O_7^{5-}$, $B_4O_9^{6-}$, $B_5O_{10}^{5-}$, and $B_{12}O_{24}^{12-}$ [13–18]. According to the

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concept of “scale chemistry” brought up by Férey, these oxo boron clusters are highly desirable for the formation of open-framework structures with large channels [19]. For example, the aluminoborate BIT-1 has a zeolitic CAN net containing extra-large 24-ring channels, while zeolites with a CAN topology only have 12-ring channels [20]. The key factor for the enlargement of the pore size of a zeolitic CAN net from 12-membered ring to 24-membered ring is the use of large B_5O_{10} clusters as structural nodes.

It has been demonstrated that oxo boron clusters are readily assembled by Al^{3+} or Ge^{4+} ions to form open-framework structures in the presence of different structure-directing agents [21,22]. In comparison, the synthesis of zinc borate zeotypes is of great challenge because 4-connected Zn^{2+} ions cannot provide enough bond valence to balance the highly negatively charged oxo boron clusters (e.g., $B_5O_{10}^{5-}$ and $B_4O_9^{6-}$) [23]. The use of amines as ligands to zinc centers can reduce Zn–O–B linkages and thus meet the local charge balance. Recently, a series of zinc borates with clusterlike, chainlike, layered, and three-dimensional structures have been prepared based on the amine-ligated strategy [24–29]. Along this line of research, here we report the solvothermal synthesis of a new inorganic-organic hybrid solid, namely, $Zn_2(dmen)_3B_{10}O_{14}(OH)_6$ (denoted SCU-5, dmen = *N*,*N*′-dimethylethylenediamine). This compound has a molecular structure containing two $B_5O_7(OH)_3$ clusters and two types of zinc–amine complexes [30]. As far as we know, such a dimeric structure has been observed for the first time in zinc borate systems.

SCU-5 was prepared by heating a mixture of $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ (0.435 g) and *N*,*N*′-dimethylethylenediamine (2.2 mL) in a 25 mL Teflon-lined stainless steel autoclave at 170 °C for 10 days. The autoclave was subsequently allowed to cool to room temperature. The product was recovered by filtration, washed with ethanol, and dried in air. Then colorless crystals were obtained in approximately 25% yield based on Zn. The powder X-ray diffraction pattern of the as-synthesized product was compared with the simulated one on the basis of the single crystal structure. The diffraction peaks on both patterns corresponded well in position, indicating the phase purity of the as-synthesized sample.

SCU-5 crystallizes in the monoclinic space group *C*2/*c* (no. 15). It has a molecular structure consisting of two zinc atoms, three dmen molecules, and two $B_5O_7(OH)_3$ clusters. The Zn(1) atom is chelated by one dmen molecule, while the Zn(2) atom is chelated by two dmen molecules. The Zn—N bond lengths are between 2.060(2) and 2.170(2) Å. Each $B_5O_7(OH)_3$ cluster contains one BO_4 tetrahedron, one BO_3 triangle, and three $BO_2(OH)$ triangles. The BO_4 tetrahedron occupies the center of the cluster and shares its oxygen vertices with four different B-centered triangles. The two $B_5O_7(OH)_3$ clusters are bridged by the Zn(dmen) complex to give rise to a dimeric structure. The $Zn(dmen)_2$ complex attaches to the dimer as a pendant (Fig. 1). The Zn–O–Zn linkage in the structure is unprecedented in amine-ligated zinc borates.

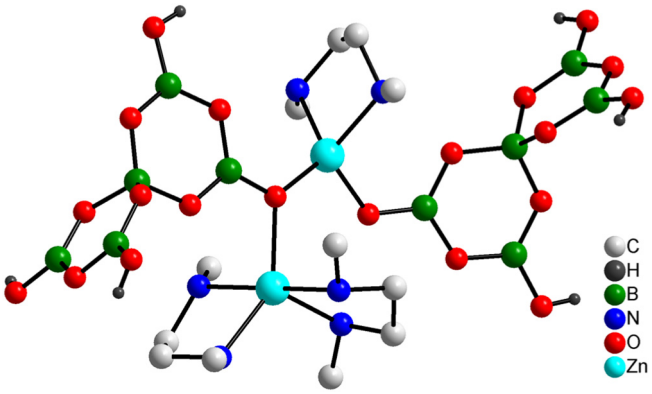

Fig. 1. View of the molecular structure of SCU-5 containing two different zinc–amine complexes.

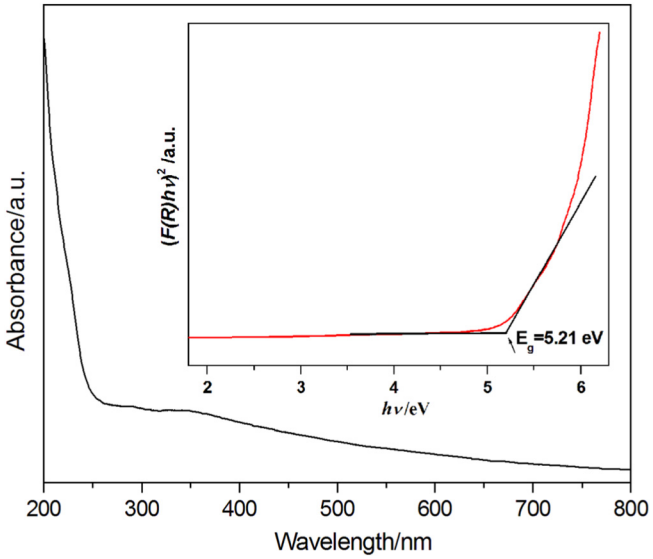

Fig. 2. The absorption spectrum of SCU-5 calculated from reflectance spectrum. Inset: a plot of $(F(R)h\nu)^2$ versus $h\nu$ for the band gap energy.

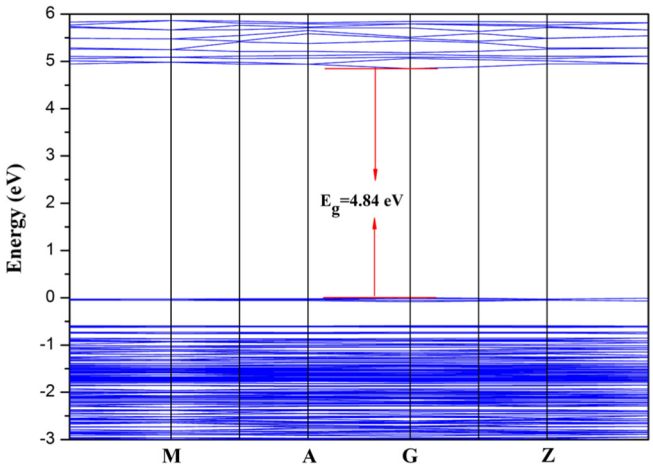

Fig. 3. Calculated band structure of SCU-5. The Fermi level is set at 0 eV.

The Zn—O bond lengths are in the range 1.888(2)–2.063(2) Å.

To date, a number of inorganic-organic hybrid zinc borates have been prepared in the presence of different amines. Interestingly, amines in these compounds tend to serve as chelating ligands or bridging ligands rather than structure-directing agents. These compounds display some interesting structural features, including the clusterlike zinc borate $[Zn(DIEN)_2][B_5O_6(OH)_4]_2$, the chainlike zinc borate $[Zn(B_4O_8H_2)(C_3H_{10}N_2)]$, the layered zinc borate $[Zn(B_4O_8H_2)(C_3H_{10}N_2)]{\cdot}H_2O$, and the three-dimensional zinc borate $[Zn_2(B_8O_{15}H_2)(C_3H_{10}N_2)_2]$ [24,25]. To the best of our knowledge, SCU-5 is the first example of a dimeric structure in the family of zinc borate materials. The structure of SCU-5 features two different zinc complexes: the Zn(dmen) complex as a cross-linker and the $Zn(dmen)_2$ complex as a pendant. Prior to this work, each inorganic-organic hybrid zinc borate only contains one type of zinc–amine complex.

The IR spectrum of SCU-5 confirms the presence of borate groups and amine molecules in the structure. The strong bands at 1354 and 1086 cm^{-1} are assigned to the asymmetric stretching vibrations of B—O of BO_3 triangles and BO_4 tetrahedra, respectively [31,32]. The band at 939 cm^{-1} belongs to the symmetric stretching vibration of B—O of the tetrahedral boron. The bands associated with the asymmetric vibrations of O—H, N—H, and C—H appear at 3387, 3258, and 2918 cm^{-1}, respectively.