Na$_2$(UO$_2$)(BO$_3$): An All-Uranium(V) Borate Synthesized under Mild Hydrothermal Conditions

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Supporting Information

**ABSTRACT:** The first entirely pentavalent uranium borate, Na$_2$(UO$_2$)(BO$_3$)$_3$, was synthesized under mild hydrothermal conditions. The single-crystal structure was solved in the orthorhombic space group Cmcm with a = 10.0472(3) Å, b = 6.5942(2) Å, and c = 6.9569(2) Å. Magnetic susceptibility measurements revealed an antiferromagnetic transition at 12 K and an effective magnetic moment of 2.33 μ$_B$. Density functional theory calculations indicated dynamic stability of the structure above 0 K.

Historically, almost all research in uranium chemistry was motivated by weapons and energy applications. More recently, however, the remediation and sequestration of legacy waste has become more pressing and is one reason for the current more comprehensive research efforts. As part of our program to prepare different classes of materials for potential use in future nuclear waste forms, we have focused on uranium borates as one class of materials that can lead to structure types practical for nuclear waste forms because uranium borates have been investigated in the past and numerous structures have been observed. As part of this effort, there exists the need to understand uranium cation stability and mobility in the environment and uranium complexation, crystal, and redox chemistry. In aqueous conditions, uranium(VI) and -4 are the most stable among the four accessible oxidation states of uranium and, thus, the most prevalent in both synthetically derived compounds and reported minerals; comparatively, uranium(V) and -(III) are considerably less stable. Reaction conditions that promote uranium(V) formation are limited, and the stability of the aqueous pentavalent [UO$_4$]$^{5-}$ species is inhibited by its tendency to either oxidize to uranium(VI) or undergo rapid disproportionation into hexavalent [UO$_6$]$^{7-}$ and tetravalent UO$_2^2+$ species. As a result of this limited stability, there are very few examples of exclusively pentavalent uranium oxides in the literature.

A primary challenge in the preparation of uranium(V) oxides lies in achieving conditions that favor the formation of exclusively uranium(V) phases over those that are mixed-valent, such as the common U$_3$O$_7$ phase. Solid-state methods have yielded ternary uranium(V) oxides, including A$_2$UO$_4$ (A = Na, K) and MU$_2$O$_5$ (M = Co, Ni). However, this method has, to date, resulted in only a handful of compositions. The preparation of uranium(V) compounds by related high-temperature methods, such as flux crystal growth, has been even less successful, although a predominantly uranium(V)-mixed-valent uranium-(V,VI) oxide of composition K$_7$U$_7$O$_{24}$ (KU$_{0.675}$O$_3$) has been reported.

The ability to prepare a desired material, such as an all uranium(V) oxide, is often greatly dependent on the specific synthetic method used. We decided to explore the hydrothermal regime to stabilize and crystallize new uranium(V) oxides, an approach that has enabled Li et al. to isolate several mixed-valent uranium(V,VI) phases as well as four exclusively uranium(V) phases, specifically the silicates K(UO)$_2$Si$_2$O$_6$ and K$_3$(UO$_2$)(Si$_3$O$_9$) and the germánates Cs$_3$UGe$_2$O$_8$ and Rb$_2$(UO$_2$)(Ge$_2$O$_7$). Utilizing the hydrothermal method for the incorporation of other oxoanions into the frameworks has also resulted in a mixed-valent uranium(V,VI) borate that has, until now, remained the only uranium(V)-containing borate. Using super- and subcritical hydrothermal conditions, we were able to prepare and isolate single crystals of the first entirely pentavalent uranium borate, Na$_2$(UO$_2$)(BO$_3$)$_3$, synthesized under mild hydrothermal conditions.

Yellow rods of Na$_2$(UO$_2$)(BO$_3$)$_3$ were prepared by adding a mixture of 1 mmol of UO$_3$ (International Bio-Analytical Industries, ACS grade), 10 mmol of NaBO$_3$·4H$_2$O (Acros Organics, 98.5%), and 2 mL of 4 M NaOH(aq) (molar ratio U:Na = 1:10.18) to a 13 cm silver ampule, which was sealed and placed in a high-pressure reactor vessel, with water added just above the fill level of the silver ampule to act as a counterpressure. Caution! Although the uranium precursor used contained depleted uranium, standard safety measures for handling radioactive substances must be followed. The reaction was heated to 300 °C for 1 day before slow cooling to 250 °C, at which point the furnace was shut off. Once cooled, the silver ampule was cut open to reveal rods of Na$_2$(UO$_2$)(BO$_3$)$_3$ along with a small quantity of a brown polycrystalline byproduct. The product mixture was sonicated in water and then methanol, followed by the manual separation of yellow rods (Figure S1). The yield of Na$_2$(UO$_2$)(BO$_3$)$_3$ was estimated to be approximately 90% based on uranium. Energy-dispersive spectroscopy analysis of the product confirmed the presence of uranium, sodium, and oxygen in the expected ratios. A suitable crystal was selected for single-crystal X-ray diffraction (XRD) analysis at 301 K, solved, and refined to an R$_1$ value of 1.52%. Relevant crystallographic data are compiled in Tables S1 and S2. A phase-pure sample of Na$_2$(UO$_2$)(BO$_3$)$_3$, as confirmed by powder XRD (Figure S2), was used for physical characterization.
property characterization. Although no reducing agent was added to the reaction, we presume that the reduction of uranium was facilitated by the formation of an in situ reducing agent, as has been frequently observed in other hydrothermal reactions.\textsuperscript{23,24} which could potentially be the silver tube itself.\textsuperscript{22}

Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) crystallizes as a layered structure in which two-dimensional uranyl borate layers are separated by sodium atoms. The planar layers of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) (Figure 1a) can be described by the uranophane anion topology and are related to a set of previously reported uranium(VI) compositions A(UO\textsubscript{2})(BO\textsubscript{3}) (A = Li, Na, K).\textsuperscript{25–27} With the exception of their corrugated rather than planar topology, these compositions exhibit uranyl borate sheets similar to those of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) (Figure S3). The two-dimensional sheets of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) (Figure 1b) are composed of chains of edge-sharing UO\textsubscript{2} polyhedra propagating along the c direction linked to neighboring chains by planar BO\textsubscript{3} groups that participate in alternating edge and corner sharing with the equatorial oxygen atoms bound to uranium. A single unique uranium site exists in a pentagonal-bipyramidal coordination environment, with equatorial oxygen bond lengths ranging from 2.319(4) to 2.481(2) Å.

The axial oxygen atoms are part of the [UO\textsubscript{2}]\textsuperscript{+} uranyl unit and exhibit an elongated bond length of 1.909(3) Å as well as an O═U═O bond angle of 173.7°. Although the uranyl bond lengths are at the shorter end of the reported values of ~1.9–2.2 Å for uranium(V) compounds, there are few uranium(V) compounds that contain uranium in a pentagonal-bipyramidal coordination; UO\textsubscript{6} polyhedra exhibiting square-bipyramidal coordination environments are the most prominent examples in the literature. The presence of [UO\textsubscript{2}]\textsuperscript{+} rather than [UO\textsubscript{2}]\textsuperscript{2+} in this structure is, in part, supported by consideration of the uranyl bond lengths of USbO\textsubscript{3}, which contains pentagonal-bipyramidal coordination of uranium with bond lengths of 1.931(7) and 2.026(3) Å.\textsuperscript{28} Thus, the uranyl bond lengths observed in Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) are quite consistent. Furthermore, the bond valence sum at the uranium site, using the parameters \(r_0 = 2.059\) and \(B = 0.37\), was calculated to be 5.08, consistent with uranium(V).\textsuperscript{29} X-ray photoelectron spectroscopy (XPS) measurements revealed broadened U\textsuperscript{V} 4f\textsubscript{7/2} and 4f\textsubscript{5/2} main peaks at 391.1 and 380.2 eV, respectively, an effect arising from multiplet splitting that is characteristic of U\textsuperscript{V}.\textsuperscript{30,31}

To investigate the magnetic properties of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}), the temperature dependence of the magnetic susceptibility was measured from 2 to 400 K at 0.1 T. The magnetic susceptibility exhibits an antiferromagnetic transition at 12 K (Figure 2).

Figure 1. (a) View of the chains of edge-sharing UO\textsubscript{2} polyhedra linked by borate groups that lie within the \([bc]\) plane and (b) structure of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) viewed along the \(c\) axis, where planar uranyl borate layers are separated by interlayer sodium cations. The yellow polyhedra represent UO\textsubscript{2}, gray triangles are BO\textsubscript{3}, and light-blue spheres are sodium atoms.

Figure 2. Field-cooled (0.1 T) magnetic susceptibility of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) measured from 2 to 400 K. An antiferromagnetic transition can be seen at 12 K.

Analysis of the inverse susceptibility data over the temperature range of 200–400 K (Figure S5) resulted in a magnetic moment of \(\mu_{\text{eff}} = 2.33\) \(\mu_{\text{B}}\), which falls within the accepted range for uranium(V) compounds of ~1.4–3.0 \(\mu_{\text{B}}\).\textsuperscript{32} Furthermore, given that the triplet-to-singlet magnetic transition characteristic of U\textsuperscript{IV} SF\textsuperscript{6} systems was not observed,\textsuperscript{33–35} magnetic measurements confirmed the presence of uranium(V) rather than uranium(IV). Below the ordering temperature, starting at 5 K, an increase in the susceptibility data is observed. Future experiments will focus on determining whether this is due to a phase transition to a paramagnetic state or due to the presence of an otherwise undetectable paramagnetic impurity.

The IR spectrum of Na\textsubscript{2}(UO\textsubscript{2})(BO\textsubscript{3}) reveals a weak broad band with a maximum at 848 cm\textsuperscript{-1} corresponding to stretching modes of the [UO\textsubscript{2}]\textsuperscript{+} unit (Figure S6); all other bands can be assigned to stretching modes of the borate group. The UV–vis spectrum also exhibits a broad absorption feature over the range of 200–470 nm, which is consistent with the electronic
transitions of the uranyl unit, along with a second broad feature centered at 500 nm, which is characteristic of charge-transfer bands of uranium(V) (Figure S7).\textsuperscript{22}

First-principles calculations were performed to assess the thermodynamic stability of Na$_2$(UO$_2$)(BO$_3$)$_2$. The calculations were carried out using the density functional theory (DFT) code Vienna Ab Initio Simulation Package,\textsuperscript{36,37} using the projector augmented plane-wave method\textsuperscript{38,39} and the Perdew–Burke–Ernzerhof generalized gradient approximation.\textsuperscript{40} The DFT calculations suggested that the structure is dynamically stable, as is indicated by the lack of negative phonon frequencies (Figure S8a). The formation enthalpy was calculated to be $-2.81$ eV, which is $0.029$ eV above the Open Quantum Materials Database\textsuperscript{41,42} generated convex hull. Although the DFT calculations show that the structure of Na$_2$(UO$_2$)(BO$_3$)$_2$ is thermodynamically metastable at 0 K, the energy difference is small, and the formation of Na$_2$(UO$_2$)(BO$_3$)$_2$ might be favored because of kinetic reasons at the synthesis temperature. Thermodynamic parameters including the entropy, heat capacity, and vibrational contribution to Helmholtz free energy as a function of the temperature were also obtained (Figure S8b). Additionally, an evaluation of the difference in the integral of the atomic-resolved projected density of states (PDOS) of Na$_2$(UO$_2$)(BO$_3$)$_2$ (Figure 3) provided information on the number of unpaired electrons in the system. Calculations suggested the presence of one unpaired electron from uranium, thus further supporting our assignment of the 5+ oxidation state of uranium in this work.

In conclusion, we have prepared Na$_2$(UO$_2$)(BO$_3$)$_2$, the first all-uranium(V) diborate, via the hydrothermal method, suggesting that this synthetic approach represents a possible route to other uranium(V)-containing systems.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00487.

Crystallographic data and refinement information, selected bond lengths, optical image of crystals, XRD pattern, topological comparisons, XPS spectrum, inverse susceptibility data, UV–vis and IR absorption spectra, thermodynamic parameters, and phonon density of states figures (PDF)

\section*{Accession Codes}
CCDC 1816157 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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\section*{Notes}
The authors declare no competing financial interest.

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